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Crevice Corrosion and the Lifetime Performance of Titanium Nuclear Waste Containers

Corrosion caverneuse et comportement pendant la durée de vie des conteneurs de déchets nucléaires fabriqués en titane

B.M. Ikeda, J.J. Noël, D.W. Shoesmith

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ABSTRACT

A multibarrier system is being proposed for the safe disposal of Canada's nuclear fuel waste. The container in which the fuel wastes are emplaced is an essential barrier and one that is expected to remain intact for at least 500 a, and possibly 10^5a. Titanium is one candidate material that has been evaluated as a potential container material. The possible localized corrosion processes which could occur on titanium have been extensively reviewed and only crevice corrosion and hydrogen induced cracking (HIC) merit consideration under Canadian waste vault conditions. HIC is dealt with in a separate report. In this report we discuss the ability to predict titanium-container lifetimes based on current crevice corrosion modeling capabilities.

An analysis of available data on the initiation, propagation and repassivation stages of crevice corrosion shows a variety of ways that titanium-container lifetime can be extended beyond the 1000-a lifetime predicted in our previously established container failure model. Crevice initiation can be avoided if vault resaturation is delayed by ~200 a, at which time the vault temperature will have fallen below 70°C. Environmental factors, i.e., oxygen content and groundwater composition, can also limit the corrosion damage. For example, the maximum pit-depth data indicates that there is not enough oxygen available in a borehole to cause penetration of the container wall by crevice corrosion. Other groundwater constituents can have either beneficial (e.g., sulphate ion as a repassivating agent) or detrimental (e.g., calcium ion as a local activating agent) effects on crevice corrosion. Alloying additions to titanium can eliminate crevice corrosion (e.g., Pd in Grade-16) or limit the extent of propagation to less than ~1 mm (Ni in Grade-12). The passive film properties are critical to maintaining the corrosion resistance of these alloys.

To justify the use of any material for construction of a nuclear fuel waste container requires a computational model to predict the time to failure. The previously reported container failure function consisted of three components: a statistical evaluation of early container failure; a low temperature hydrogen induced cracking failure mode; and a temperature dependent crevice corrosion failure mode. This model predicted lifetimes >1000 a for 99.9% of the containers in the disposal vault. An independent assessment of corrosion damage based on the empirical relationship between maximum penetration depth due to crevice corrosion and oxygen consumption agreed with the predictions of the container failure function. Although neither model includes time-dependent oxygen depletion, both models provide defensible upper bounds on the effect of oxygen (trapped in the disposal vault) on container performance.

The data requirement for establishing the crevice corrosion limits of Grades-2, -12 and -16 titanium and for improving the arguments for the long lifetime prediction are presented. An extensive database including critical oxygen concentration for repassivation and penetration depths at different temperatures, and a coupling with mass transport calculations are required to predict the duration of crevice corrosion and the maximum damage expected. Passive-film properties of Grades-12 and -16 are required to determine the protective nature of the film and justify the long-term predictions of crevice corrosion resistance.

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CORROSION CAVERNEUSE ET COMPORTEMENT PENDANT LA DURÉE DE VIE DES CONTENEURS DE DÉCHETS NUCLÉAIRES FABRIQUÉS EN TITANE

par

B.M. Ikeda, J.J. Noël et D.W. Shoesmith

RÉSUMÉ

Un système comportant des barrières multiples est proposé pour le stockage sûr des déchets de combustible nucléaire du Canada. Le conteneur dans lequel les déchets de combustible sont mis en place constitue une barrière essentielle, et celle-ci devrait demeurer intacte pendant au moins 500 a et éventuellement 10^5 a. Le titane a été évalué comme un métal de fabrication possible des conteneurs. Les phénomènes de corrosion localisés éventuels qui pourraient se produire sur le titane ont été examinés de manière approfondie, et seules la corrosion caverneuse et la fissuration due à l'hydrogène méritent d'être prises en compte dans les conditions de l'enceinte de stockage des déchets canadienne. La fissuration due à l'hydrogène fait l'objet d'un rapport distinct. Dans le présent rapport, les auteurs examinent la capacité de prévoir la durée de vie des conteneurs en titane en fonction des possibilités actuelles de modélisation de la corrosion caverneuse.

Une analyse des données dont on dispose sur les stades d'amorçage, de propagation et de repassivation de la corrosion caverneuse indique divers moyens par lesquels la durée de vie des conteneurs en titane peut être prolongée au-delà de la durée de vie de 1 000 a prévue par notre modèle de rupture des conteneurs élaboré antérieurement. L'amorçage de la fissuration peut être évité si la resaturation de l'enceinte est retardée de ~ 200 a; à ce moment, la température de l'enceinte aura baissé au-dessous de 70 °C. Les facteurs liés à l'environnement, c'est-à-dire la teneur en oxygène et la composition des eaux souterraines, peuvent également limiter les dégâts dus à la corrosion. Par exemple, les données relatives à la profondeur de piqûration maximale indiquent qu'il n'y a pas suffisamment d'oxygène dans un trou de forage pour provoquer la pénétration de la paroi du conteneur par corrosion caverneuse. D'autres constituants des eaux souterraines peuvent avoir des effets soit favorables (p. ex., ions sulfates comme agent de repassivation), soit défavorables (p. ex., ions calcium comme agent activant local) sur la corrosion caverneuse. L'ajout d'éléments d'alliage au titane peut éliminer la corrosion caverneuse (p. ex., le Pd dans le titane de nuance 16) ou en réduire la propagation à moins de ~ 1 mm (Ni dans le titane de nuance 12). Les propriétés de la pellicule passive sont cruciales pour conserver la résistance à la corrosion de ces alliages.

Afin de justifier l'emploi d'un matériau, quel qu'il soit, pour la fabrication d'un conteneur de déchets de combustible nucléaire, on doit disposer d'un modèle de calcul qui permette de prévoir quand la rupture se produira. La fonction de rupture des conteneurs qui a été communiquée antérieurement comprenait trois éléments : une évaluation statistique de la rupture prématurée des conteneurs; un mode de rupture par fissuration due à l'hydrogène à basse température; et un mode de rupture par corrosion caverneuse variant selon la température. Ce modèle prévoyait une durée de vie > 1 000 a dans le cas de 99,9 % des conteneurs dans l'enceinte de stockage permanent. Une évaluation indépendante des dégâts dus à la corrosion fondée sur la relation empirique entre la profondeur de pénétration maximale attribuable à la corrosion caverneuse et la consommation d'oxygène concordait avec les prévisions de la fonction de rupture des conteneurs. Bien que ni l'un ni l'autre des modèles ne tienne compte de l'appauvrissement en oxygène en fonction du temps, les deux modèles offrent des limites supérieures défendables quant à l'effet de l'oxygène (emprisonné dans l'enceinte de stockage permanent) sur le comportement des conteneurs.

Les auteurs énoncent les données nécessaires pour établir des limites de corrosion caverneuse du titane de nuances 2, 12 et 16, et étayer les arguments de prévision d'une longue durée de vie. Il faut établir une base de données considérable comprenant la concentration en oxygène critique pour la repassivation et les profondeurs de pénétration à différentes températures, et un lien avec les calculs de transport de masse en vue de prévoir la durée de la corrosion caverneuse et les plus grands dégâts auxquels on peut s'attendre. Il faut également établir les propriétés de la pellicule passive du titane de nuances 12 et 16 afin de déterminer les caractéristiques de protection offertes par cette pellicule et de justifier les prévisions à longue échéance de la résistance à la corrosion caverneuse.

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CONTENTS

1. INTRODUCTION

In the Canadian Nuclear Fuel Waste Management Program, a multibarrier system is being proposed for the safe disposal of Canada's nuclear fuel waste in plutonic rock of the Canadian Shield (Johnson et al. 1994a). The corrosion-resistant container in which the used fuel waste is to be emplaced is an essential barrier. Two candidate materials, copper and titanium, have been studied as potential container materials. The reasons for selecting these materials have been discussed elsewhere (Johnson et al. 1994a). To date, titanium has been evaluated for the borehole emplacement scenario (Shoesmith et al. 1996), but its behaviour would not be expected to be significantly different for in-room emplacement. The durability and corrosion resistance of titanium in many aggressive environments has been frequently demonstrated and reviewed in detail (Ikeda and Shoesmith 1997). The possible localized corrosion processes which could occur on titanium have also been extensively reviewed (Shoesmith and Ikeda 1997) and only crevice corrosion and hydrogen induced cracking (HIC) merit consideration under Canadian waste vault conditions.

Figure 1 shows the expected evolution of vault conditions and the possible corrosion scenarios which could occur if a grade of titanium susceptible to crevice corrosion were to be used.

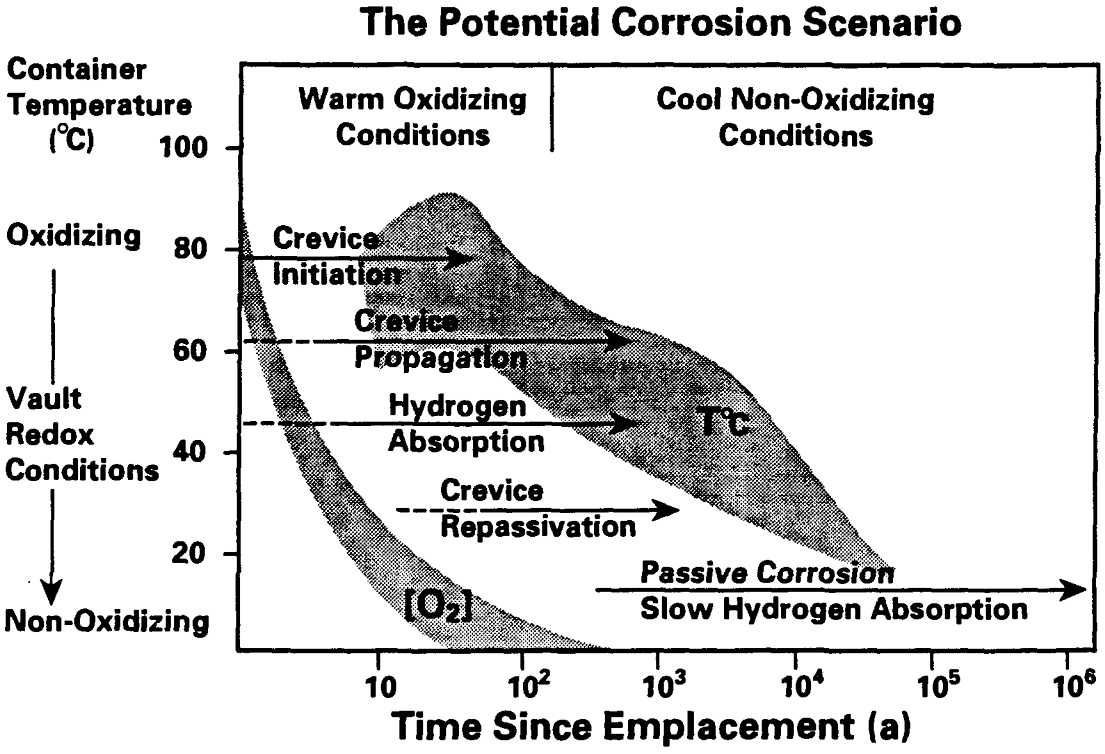

FIGURE 1: The Expected Evolution of Vault Conditions and the Potential Corrosion Failure Modes Associated with each Period

The processes of crevice corrosion and hydrogen absorption are inextricably linked and two paths to container failure can be envisaged, Figure 2. If crevice corrosion propagates unchecked then both the depth of wall penetration and the extent of hydrogen absorption into the metal will increase rapidly. The rate of hydrogen absorption is related to the rate of crevice propagation. Once checked by repassivation, however, both wall penetration and hydrogen absorption will continue much more slowly under general passive conditions. Eventual failure will occur when either the depth of wall penetration exceeds the corrosion allowance or the amount of hydrogen absorbed exceeds the critical hydrogen concentration, Figure 2. Clearly, whatever the eventual mode of failure, the rate and extent of crevice corrosion will have a major impact on the time to failure of the container.

Recently, we reviewed the effect of hydrogen absorption on the lifetime performance of titanium containers (Shoesmith et al. 1997), and the consequences for failure times by HIC. In this report we review our studies on the crevice corrosion of titanium alloys. The factors controlling the initiation of crevice corrosion will be described and used to assess the likelihood that this mode of corrosion will occur under waste vault conditions. Many factors influence the rate of propagation of crevice corrosion and much of this information has been published elsewhere (Shoesmith et al. 1995b). Here, we will only summarize these influences. The modeling procedures developed to predict the consequences of crevice propagation on container lifetimes and the most propitious ways to limit crevice corrosion, and hence extend lifetimes, are discussed.

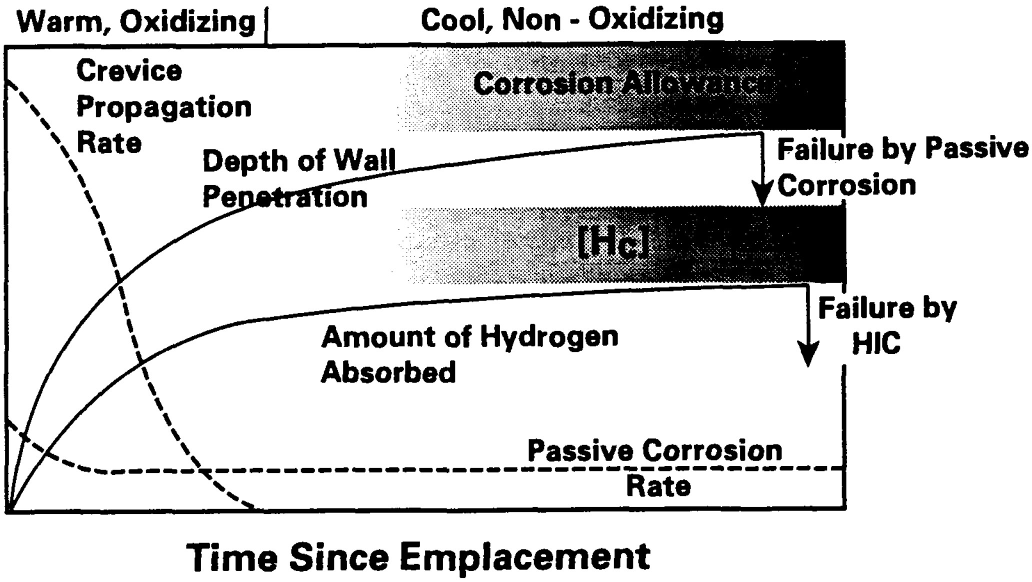

FIGURE 2: Schematic Showing the Expected Variations in the Rates of Crevice and Uniform Passive Corrosion and the Extent of Hydrogen Absorption with Time as Vault Conditions Evolve from Initially Warm and Oxidizing to Eventually Cool and Non-oxidizing. The relationships between these parameters and the depth of wall penetration compared with the engineered corrosion allowance and the critical value for HIC are also shown.

1.1 CRITERION FOR CONTAINER FAILURE BY CREVICE CORROSION

The criterion for container failure by crevice corrosion is illustrated in Figure 3. To prevent failure by buckling, a minimum of 2 mm of wall thickness is required, assuming a uniform loading of 10 MPa hydrostatic pressure will be acting externally on the container (Teper 1992). Consequently, if crevice corrosion were to thin the container wall to less than 2 mm in an area unsupported (because of a void in the particulate filling the container), then the strain at that site could exceed the critical strain and mechanical failure would occur (Teper 1992, Johnson et al. 1994b). The specific criteria (i.e., critical width, critical strain, Figure 3) for mechanical failure of the reference thin-shell, packed-particulate container have been discussed elsewhere (Johnson et al. 1994a). For a container design with a much more rigid internal structure (e.g., a thick carbon steel support) the need to reserve 2 mm of the total titanium shell wall thickness to avoid mechanical failure would not be required. Failure of the titanium shell would then occur when either the deepest penetration exceeded the full wall thickness or the hydrogen content exceeded the critical amount for brittle fracture.

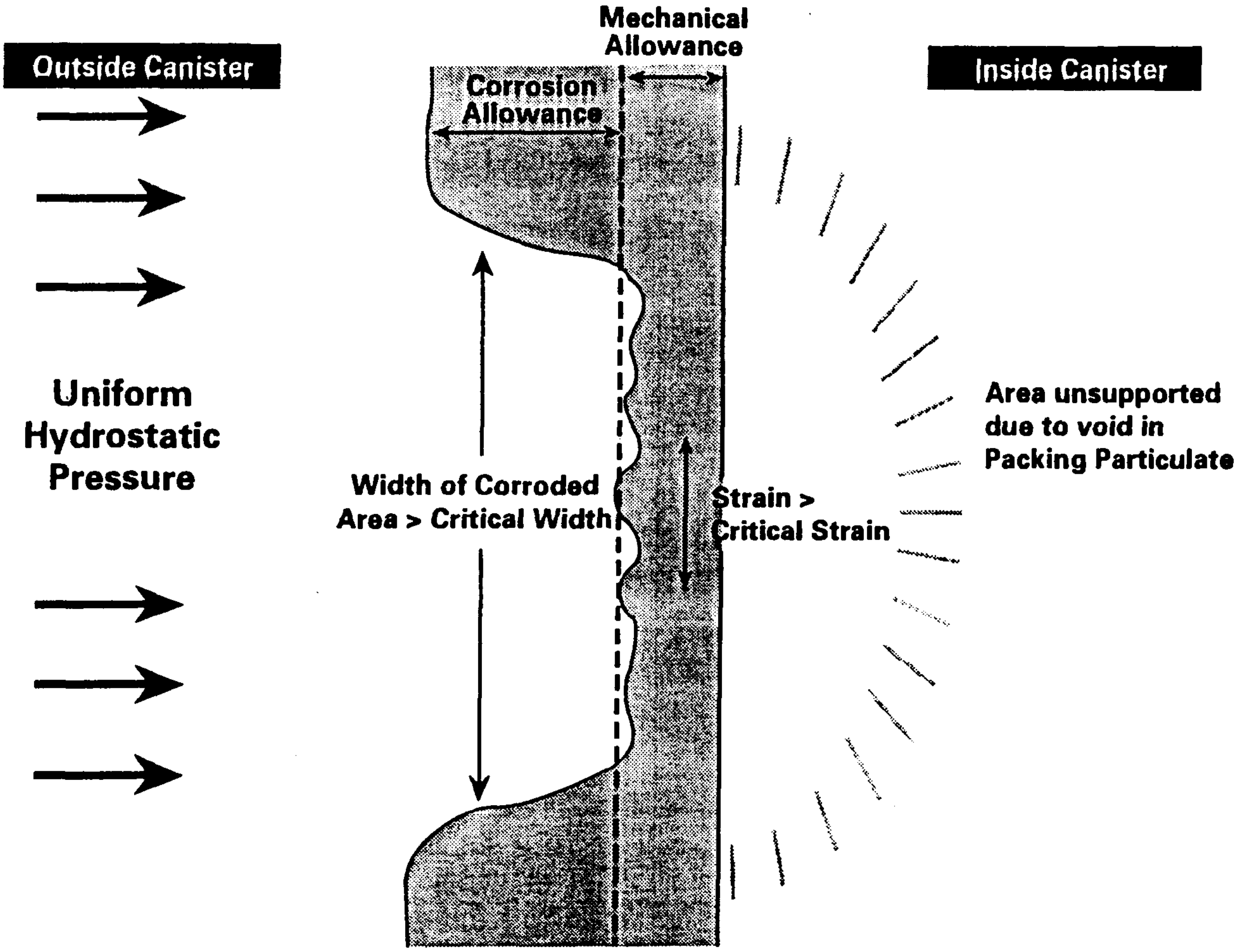

FIGURE 3: Schematic Showing the Form of Crevice Corrosion and its Relationship to the Mechanical Conditions Leading to Container Failure

1.2 SUSCEPTIBILITY TO CREVICE CORROSION

According to Schutz and Thomas (1987), crevice attack of titanium alloys will not occur below a temperature of 70°C, regardless of solution pH or chloride concentration. This claim is based on the pH and temperature limits determined for various alloys in saturated sodium chloride brines, and is supported by decades of industrial experience. These conditions are relevant to expected Canadian waste vault conditions because saline groundwaters have been encountered in the Canadian Shield (Gascoyne 1988). If we accept this criterion, and if crevice initiation could be prevented until container wall temperatures fall to <70°C then we could dismiss this corrosion process as a feasible failure mechanism. From calculations of container cooling profiles under saturated conditions we can calculate, for the borehole emplacement design, that 60% of all containers will have met this temperature criterion of Schutz and Thomas after only 30 a and all the containers will have met this criterion after 200 a (Shoesmith et al. 1996).

Unsaturated conditions will exist in a borehole at short times when heat from the container drives moisture away from the container surface. Crevice corrosion is extremely unlikely under these conditions (Shoesmith and Ikeda 1997) and its initiation will be delayed by the duration of the unsaturated period. Therefore, crevice corrosion could be eliminated altogether if unsaturation persists long enough for container temperatures to decay to <70°C. Unfortunately, to date it has proven very difficult to predict this period for resaturation with any certainty. Present estimates range from <100 a to >1000 a (Andrews et al. 1986, Pusch et al. 1985, Thomas and Onofrei 1996).

2. CONDITIONS FOR THE INITIATION OF CREVICE CORROSION

In our recent studies we have confirmed the validity of the Schutz and Thomas temperature guideline. Using our galvanic coupling technique (Ikeda et al. 1985), the potentials of planar (E_P) and artificially-creviced (E_C) Grade-2 titanium electrodes in aerated 0.27 mol·L^{-1} NaCl were compared as the temperature was increased in stages, Figure 4A. While slightly different, both E_P and E_C increased in an identical way until T = 72°C was reached (67°C for Grade-12 titanium, not shown) when the two potentials separated. The fall in E_C is the expected behaviour for crevice initiation, and this was accompanied by the onset of current flow (I_C) through the zero resistance ammeter connecting the creviced electrode to a large titanium counter electrode. Subsequently, for both Grade-2 titanium and Grade-12 titanium (Table 1), current "noise" transients attributable to localized events such as film breakdown processes within the crevice were recorded, Figure 4B.

Other experiments with creviced electrodes were performed in which the temperature was raised rapidly to 100°C, but the experiment halted before the initiation of crevice corrosion. Subsequent inspection of the crevice surfaces showed general etching of the metal surface within the occluded area in experiments performed in both 0.27 mol·L^{-1} NaCl and "chloride free" 0.14 mol·L^{-1} Na_2SO_4 solutions. While the initiation of crevice corrosion inevitably occurred in chloride solutions, several weeks of exposure did not lead to crevice initiation in sulphate

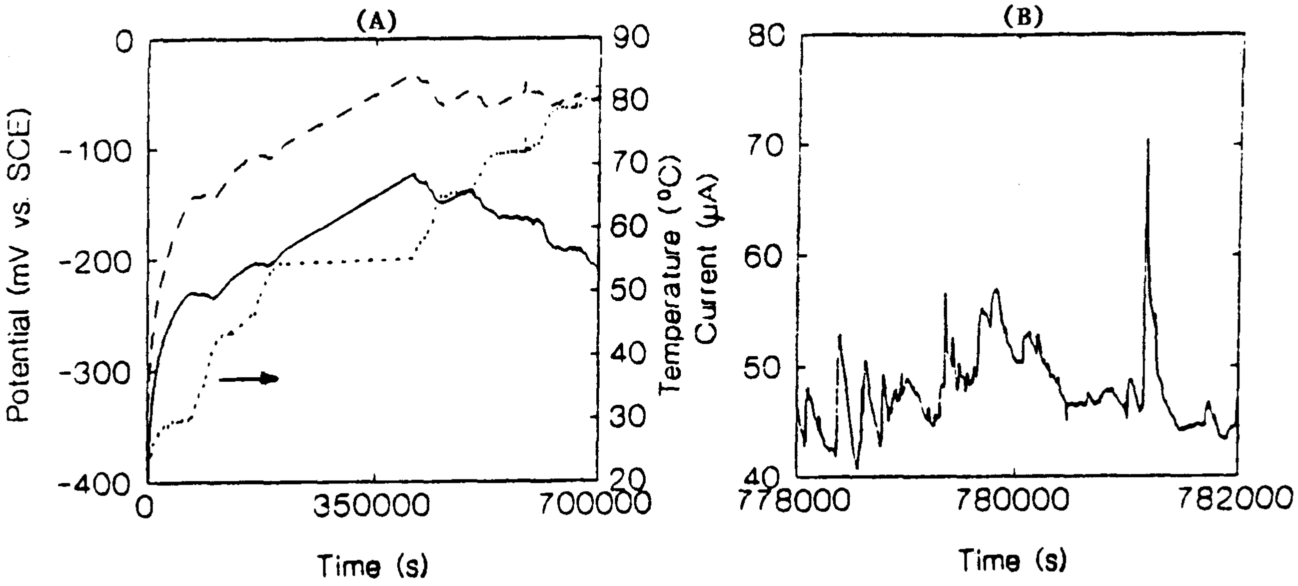

FIGURE 4: Electrochemical Data Showing the Temperature Dependent Behaviour of Artificially Creviced Grade-2 Titanium Electrodes Exposed to 0.27 mol·dm^{-3}.

A) Crevice Electrode Potential (———), Planar Electrode Potential (— — —) and Temperature (• • •) as a function of time.

B) Current "noise" transient observed after the crevice and planar electrode potentials have begun to diverge, indicating crevice corrosion has begun.

TABLE 1

COMPOSITION OF TITANIUM ALLOYS

Grade	Composition /wt.%							
	N	C	H	Fe	O	Ni	Mo	Pd
2	0.03	0.10	0.015	0.30	0.25			
12	0.03	0.10	0.015	0.30	0.25	0.6-0.9	0.2-0.4	
7	0.03	0.10	0.015	0.30	0.25			0.12-0.25
11	0.03	0.10	0.015	0.20	0.18			0.12-0.25
16	0.03	0.10	0.015	0.30	0.25			0.04-0.08

solutions. Similar etching has also been observed on the freely exposed surfaces of severely crevice-corroded coupons in regions adjacent to the crevice where acidic solution from the crevice interior flowed out over the surrounding surfaces. The observed etching pattern is a clear indication of the occurrence of a film thinning process. One can conclude that a passive dissolution process caused by the general (not localized) development of acidity within the occluded region precedes the initiation of crevice corrosion. This is consistent with the results of Blackwood et al. (1994), which show that the dissolution of oxide films on titanium occurs generally, not locally. That film thinning is necessary before initiation can occur also indicates that the Cl⁻ ion responsible ultimately for film breakdown cannot traverse the oxide.

Two questions remain unanswered: (i) what is the source of acidity leading to passive dissolution; and (ii) why is a temperature of ~70°C required for crevice initiation? Recently, we have reviewed the properties of passive films on titanium and how they are affected by positive and negative polarization, pH and temperature (Shoesmith and Ikeda 1997). Various studies have demonstrated that the nature of the film growth process on titanium changes with temperature. At low temperatures, passive film growth occurs via the standard high-field ion-conduction process and the passive film formed is thin and very protective. As the temperature increases to >60°C film breakdown and recrystallization occurs. We have demonstrated by impedance measurements that this breakdown/recrystallization process has an adverse effect on the protective properties of the passive oxide. Figure 5 shows a clear decrease in the resistance

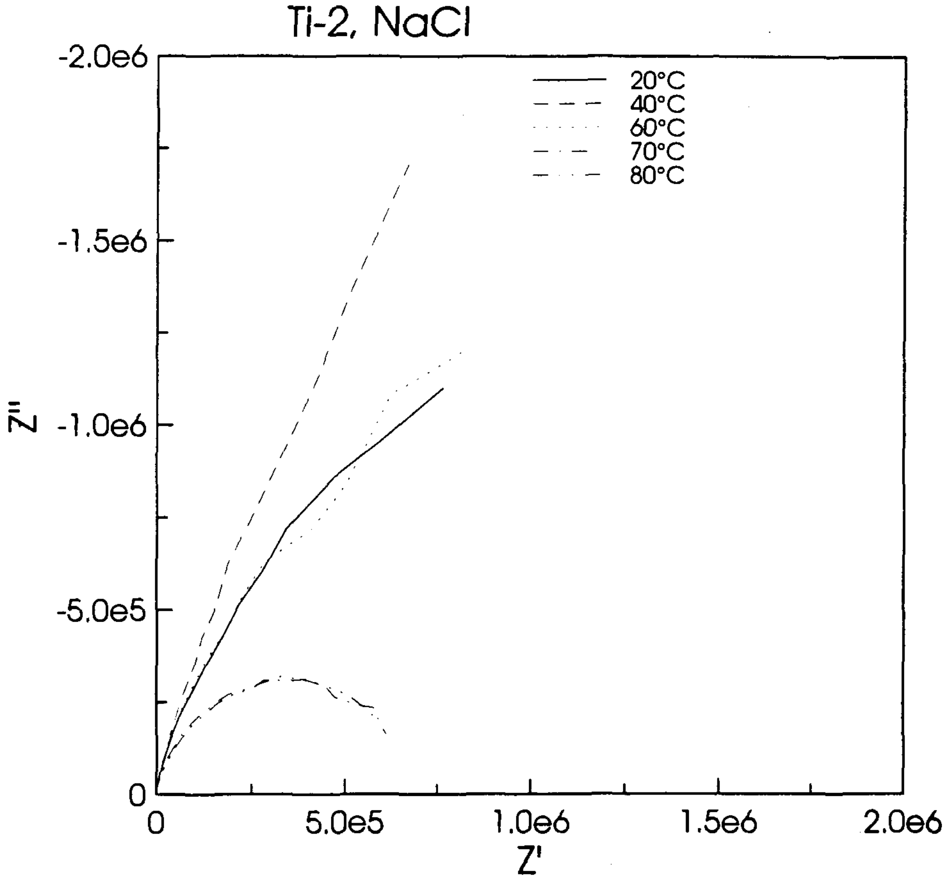

FIGURE 5: Impedance Data Showing the Change in Film Properties with Increasing Temperature. The semi-circular loci observed at the higher temperatures indicates a porous layer whilst the linear loci observed at lower temperatures indicates an integral resistive layer.

of the passive film[1] as the temperature rises above 60°C. A more complete discussion of these impedance measurements will be published elsewhere.

Film breakdown and recrystallization lead to the introduction of a large density of grain boundaries which act as short diffusion pathways for the ions involved in film growth. Consequently, film growth is accelerated and some metal dissolution occurs. Hydrolysis of the dissolved metal cations leads to local acidification of the solution. Under non-occluded (i.e., planar) conditions this does not matter since the rate of production of protons is slow and they are rapidly transported to the bulk solution. However, for crevice conditions, transport losses are minimized and a low pH is gradually established leading to film dissolution and the initiation of local breakdown sites which eventually coalesce into general crevice corrosion. An attempt to represent this situation schematically is shown in Figure 6.

3. PROPAGATION OF CREVICE CORROSION

The crevice corrosion process for titanium has been studied extensively, particularly for Grades-2 and -12 (Schutz and Thomas 1987, Shoesmith et al., submitted). An oxygen concentration cell (oxygen is depleted within the crevice but not outside it) is established during active crevice propagation on titanium (Figure 6). Oxygen reduction in the high oxygen concentration environment outside the crevice drives metal oxidation: on the exterior surfaces this leads to solid-state oxide growth, but in the reducing acid environment within the crevice, to titanium dissolution. The cationic titanium species in the crevice solution are rapidly hydrolyzed to produce protons and oxide. The decreasing pH within the creviced region leads to further destabilization of the protective oxide film, and an increase in the rate of titanium dissolution accompanied by a further decrease in crevice pH. With decreasing pH, proton reduction within the crevice environment becomes feasible. This reaction can then couple with the metal oxidation reaction and increase the overall rate of metal dissolution. Precipitation of the oxide from the acidified reducing environment within the crevice constricts the crevice ensuring that the crevice gap does not increase as the metal surface dissolves.

Proton reduction within the crevice will generate atomic hydrogen on the metal surface. Some of this hydrogen will combine to produce the hydrogen gas that can be seen bubbling from the mouth of a rapidly propagating crevice. Approximately 10-20% of the hydrogen generated on the crevice-corroding surface will be absorbed into the metal and then diffuse through the metal away from the crevice surface (Noël et al. 1996). This absorbed hydrogen reacts with titanium to produce a brittle titanium hydride precipitate, large quantities of which transform titanium from a ductile to a brittle material. At hydrogen concentrations less than that required for embrittlement, high stress fields can force a crack to slowly propagate between regions of ductile metal and brittle hydride prior to fast crack growth through the brittle phase. Clearly, extensive crevice

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[1] The electrode/electrolyte interface is electrically analogous to a resistor and capacitor in parallel. A plot of the real (Z′) and imaginary (Z″) components of electrical impedance should trace a semicircle, with a radius equal to the resistance. Figure 5 shows that at low temperatures, Z″ is nearly proportional to Z′, suggesting a very large semicircle, and large resistance.

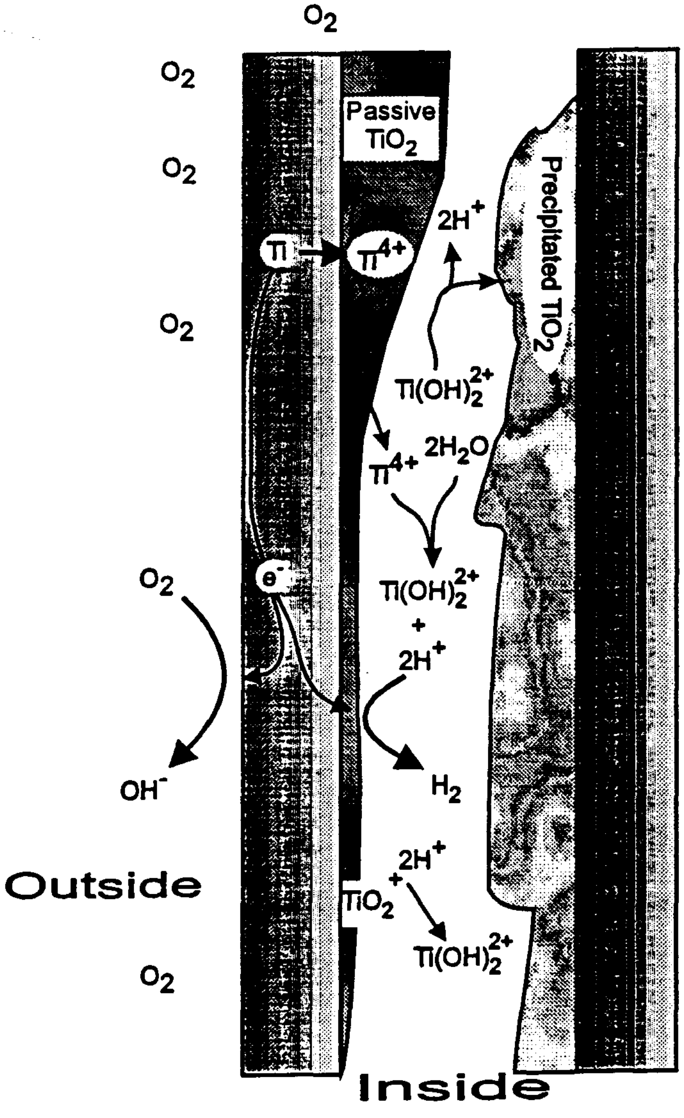

FIGURE 6: Schematic Diagram Showing the Chemical and Transport Properties for Crevice Corrosion of Grade-2 Titanium

propagation could lead to a hydrogen concentration sufficient to render the material susceptible to hydrogen induced cracking. The potential for failure by hydrogen induced cracking has been discussed elsewhere (Shoesmith et al. 1997).

The use of titanium can be justified in many industrial environments, even in the presence of crevices (Ikeda and Shoesmith 1997). Within the scope of our program, a large number of the parameters that control the crevice propagation reaction have been studied. These include temperature, oxygen concentration, chloride concentration, groundwater composition, heat treatment and welding, materials impurity and alloying additions, and radiation. Here we will review these effects. Since, in a number of cases, extensive discussions have been published elsewhere, these reviews will be quite brief.

3.1 TEMPERATURE

The effect of temperature on crevice corrosion depends upon the material composition. Commercially pure grades of titanium, such as Grade-2, have a crevice corrosion rate that increases with increasing temperature between room temperature and 150°C (Ikeda et al. 1990b). In the presence of an essentially constant oxygen concentration, the rate of crevice corrosion follows an Arrhenius dependence and crevice corrosion, once initiated at elevated temperatures, continues to propagate at temperatures as low as 25°C. If it is assumed that the oxygen concentration remains constant and that the rate is not time dependent, then this Arrhenius relationship can be used, along with the calculated temperature-time profiles for containers in a waste vault, to predict the crevice corrosion rates as a function of container emplacement time (Shoesmith et al. 1995b, Johnson et al. 1994a).

The crevice corrosion rate for Grade-12 titanium is independent of temperature between 70 and 150°C (Ikeda et al. 1990b). Spontaneous repassivation occurs at all temperatures studied with the repassivation time decreasing with increasing temperature. Consequently, little corrosion is observed at 150°C. The maximum amount of crevice corrosion is observed at ~125°C. If crevice corrosion is initiated at temperatures >75°C and the temperature then slowly decreased, spontaneous repassivation is observed at temperatures below ~65-70°C. As discussed in section 2 above, the passive film changes from a contiguous amorphous barrier to a crystalline but cracked structure at a temperature near 70°C (Shoesmith et al., submitted). The change in film structure leads to metal dissolution which can result in localized acidification. The acidification leads to oxide film dissolution and the eventual development of initiation sites for localized attack (Shoesmith and Ikeda 1997). Repassivation, if it occurs, will reform the passive layer, which will not be porous if the repassivation temperature is lower than the initiation temperature. The observation that repassivation occurs at the same temperature for different experimental conditions and the argument that both crevice initiation and repassivation should depend on film recrystallization strongly suggest a critical repassivation temperature near 70°C. However, the possible role of either a critical oxygen concentration or some material property (e.g., critical surface nickel concentration) has not been studied extensively.

The critical repassivation temperature defines a temperature below which crevice corrosion will cease to propagate (Tsujikawa and Kojima 1991). Thus the extent of crevice corrosion damage will be limited by repassivation as the container temperature decreases. If we accept that repassivation is inevitable for $T \lesssim 70°C$, then, for Grade-12 titanium, crevice propagation can continue for a maximum period of ~200 a for the reference vault design in Johnson et al. (1994a) and the maximum extent of crevice corrosion damage will be limited. However, it is likely that crevice repassivation will occur rapidly, even at temperatures above 70°C, as observed in our experiments. If this is the case, then crevice corrosion damage should be minor. Those containers whose surface temperature never exceeds 70°C should experience no crevice corrosion damage. The possibility of failure of Grade-12 titanium by crevice corrosion is, therefore, extremely remote and container lifetimes $>10^5$ a should be achievable (Shoesmith et al. 1995a).

3.2 CHLORIDE CONCENTRATION

Grade-2 titanium is unusual in that the extent of crevice corrosion decreases with increasing chloride concentration (Bailey et al., 1996). The diminished attack at higher (compared with lower) chloride concentrations is thought to be due to either a diminished potential difference between the creviced and external surfaces, or to an increased crevice pH caused by chloride complexation of Ti^{4+} which prevents its hydrolysis to produce acidity. The distribution of corrosion damage at 5 $mol{\cdot}L^{-1}$ NaCl concentration is more uniform than at lower concentrations suggesting a decreased driving force for localized attack. The influence of other complexing anions (e.g., SO_4^{2-}) on crevice corrosion supports the role of titanium-chloride complexation in inhibiting crevice propagation (Shoesmith et al. 1995b).

For materials which resist crevice initiation, e.g., high iron containing Grade-2 titanium or Grade-12 titanium, the maximum extent of crevice corrosion occurs at a chloride concentration of ~2-3 $mol{\cdot}L^{-1}$ NaCl for temperatures between 100-150°C. Increasing the chloride concentration increases the probability of initiation but, at higher chloride concentrations, the inability to sustain propagation diminishes the overall extent of corrosion. The maximum depth of corrosion penetration at any chloride concentration under the fully aerated conditions used in our experiments is ~1 mm. This indicates that chloride concentration is not the important limiting factor in the overall corrosion performance of a Grade-12 titanium waste container.

3.3 OXYGEN CONCENTRATION

Crevice corrosion on titanium requires the availability of oxygen outside the crevice in order to drive metal dissolution inside the crevice. For susceptible materials, such as Grade-2 titanium, an unlimited supply of oxygen in the bulk environment could result in sustained crevice corrosion leading to extensive damage. In a closed system where oxygen can be depleted, the extent of crevice corrosion will be limited by the total amount of available oxygen. Increasing the oxygen concentration increases the steady-state propagation rate, and does not appear to induce repassivation. However, at sufficiently low oxygen concentrations, the dissolution reaction slows to a rate where the loss of protons (by diffusion out of the crevice) can cause an increase in crevice pH. This causes a cascade effect, the increasing pH leading to a further decrease in metal oxidation rate, and, for a critical low oxygen concentration, spontaneous crevice repassivation (Ikeda et al. 1990b).

The total extent of corrosion damage and the steady-state crevice corrosion rate on Grade-12 titanium are independent of the initial oxygen concentration. The initial increase in rate with increasing oxygen concentration (Figure 7) is balanced by a decrease in crevice repassivation time. The potential (a measure of the reactivity of the material in that exposure environment) of an active crevice electrode and a planar electrode were not sensitive to the oxygen partial pressure. These results suggest that oxygen reduction does not control the crevice corrosion reaction on Grade-12 titanium as observed for Grade-2 titanium.

Environmental variables such as oxygen partial pressure do not influence the extent of corrosion of Grade-12 titanium suggesting that a container fabricated from this material would suffer only

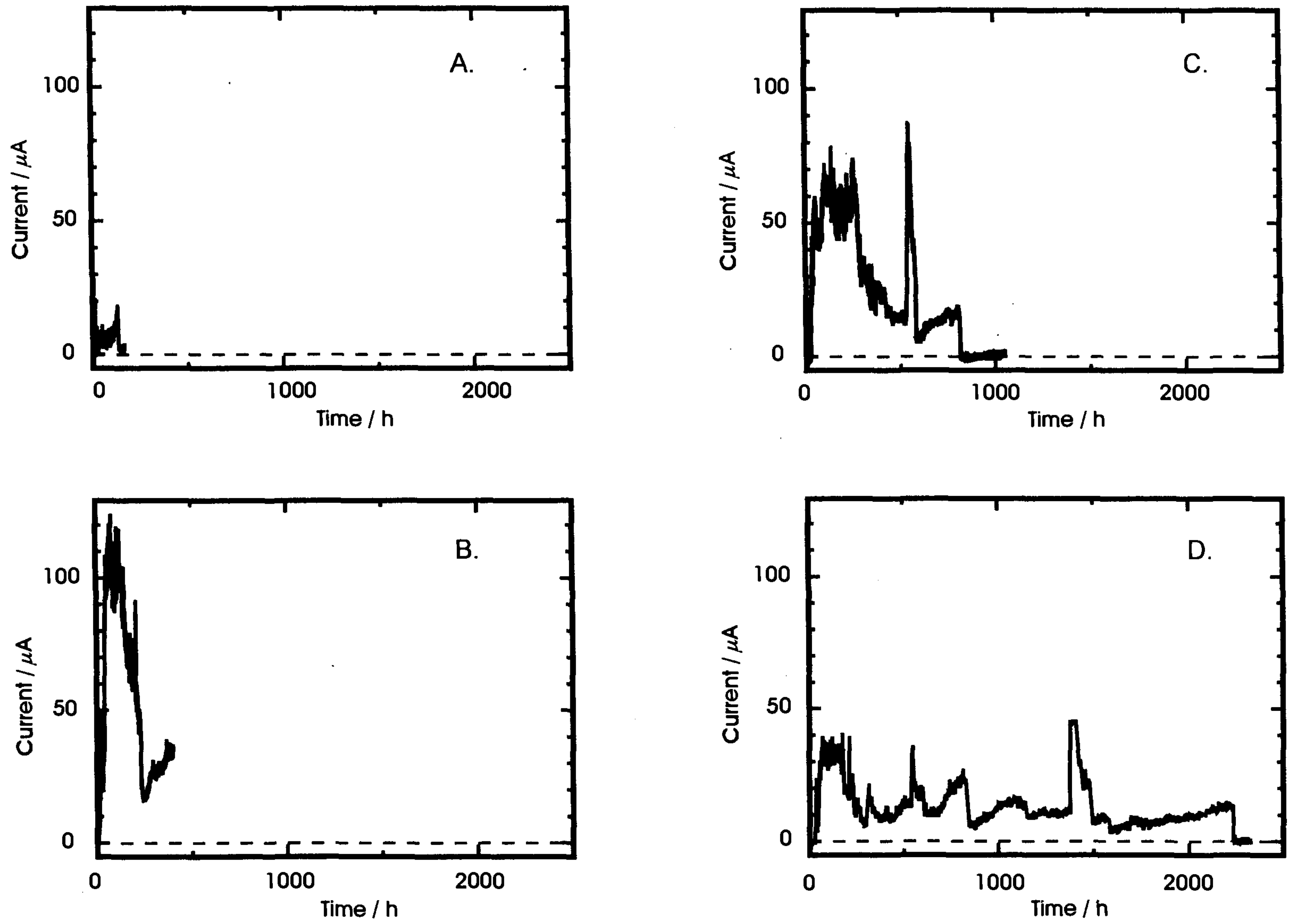

FIGURE 7: Coupled Crevice Current Data For Grade-12 Titanium Exposed to Various Oxygen Atmospheres: A. 73 psi; B. 33 psi; C. 13 psi; D. 3 psi

limited crevice corrosion regardless of the salinity, temperature or oxygen concentration at the time of emplacement.

3.4 GROUNDWATER COMPOSITION

While the temperature, oxygen concentration and chloride concentration are the environmental parameters dominating the crevice corrosion process, other groundwater species can influence the crevice propagation rate. Many of these species will be present naturally in the native groundwater whilst others will be introduced, concentrated or removed as a consequence of contact with other engineered barriers, specifically the clay and sand in the buffer/backfill materials. An extensive discussion of the influence of groundwater composition on the crevice corrosion rate and maximum depth of penetration has already been given and will only be briefly summarized here (Shoesmith et al. 1995b).

Many of the commonly observed solution species will influence crevice corrosion through their impact on local acidification. The groundwaters of the Canadian Shield are predominantly Na/Ca chloride containing waters, and contain very little Mg. At 150°C, low Ca concentrations depress the crevice corrosion rate, but higher concentrations accelerate the rate relative to a NaCl solution with a similar chloride concentration. The hydrolysis of Ca^{2+} at 150°C is sufficiently strong that concentration of calcium within the crevice can result in localized pockets of low pH and the subsequent generation of pits within the creviced region. The maximum depth of these localized penetrations appears to be limited, possibly by a combination of i) polarization effects (i.e., IR drop down the crevice) and ii) transport processes required to maintain the locally low pH. The Ca^{2+} present in the groundwater will be supplemented by dissolution of gypsum, $CaSO_4$, and calcite, $CaCO_3$, present in the clay buffer surrounding the container (Lemire and Garisto 1989).

Sulphate and carbonate have been found to inhibit crevice corrosion by influencing those processes leading to the acidication of the crevice. Experiments using chloride-containing-buffer slurries indicate an increased concentration of $CaSO_4$ and a decreased rate and extent of crevice corrosion. This suggests that of the species leached from the clay, the sulphate ion dominates the crevice chemistry.

The vault environment will contain copious amounts of silica, both in the form of sand added to the environment, and the rock mass itself. Silica containing species are known to influence corrosion of many other systems, and studies on titanium indicate that silica will inhibit crevice corrosion (Shoesmith et al 1995b). Thus, in a series of immersion experiments in which crevices were exposed to various chloride containing solutions at temperatures up to 150°C, crevice corrosion was not observed when the experiments were performed in glass vials but did occur when performed in titanium vessels with or without PTFE-liners. Subsequently, these results were confirmed in an electrochemical experiment performed in a titanium vessel at 100°C using an NaCl solution containing crushed glass. The results indicated a sluggish initiation, a low propagation rate, and an early repassivation before all the oxygen had been consumed. The total extent of crevice propagation, as indicated by weight change, was small. This is in contrast to the behaviour observed in a similar experiment performed in the absence of crushed glass, is consistent with the lack of corrosion observed in glass vial tests, and is a clear indication that silica will limit the extent of crevice corrosion damage.

The groundwater compositions observed in the Canadian shield should not be significantly detrimental to the crevice corrosion performance of Grade-2 titanium. Further beneficial effects will result from the conditioning of the groundwater by the clay and sand placed next to the container. The leached species may inhibit the crevice corrosion process for sufficiently long that the temperature of the container could fall below the critical crevice initiation temperature.

3.5 ALLOYING AND IMPURITIES EFFECTS

Iron, nickel and palladium are commonly added to titanium, the latter two specifically to increase crevice corrosion resistance. The effect of these elements on crevice corrosion has been demonstrated (Ikeda et al., 1994) and recently reviewed (Shoesmith et al., submitted). For experiments conducted on Grades-2, -12, and -16 titanium (Table 1) the extent of crevice corrosion damage increases in the order:

Grade-16	<<	Grade-12	<	Grade-2	<	Grade-2	<	Grade-2
(Pd)		(Ni and Mo)		(high Fe and Ni)		(high Fe, low Ni)		(low Fe and Ni)

These elements are essentially insoluble in titanium, forming intermetallic phases or stabilizing the β-phase at grain boundaries. The palladium-containing intermetallics exhibit electrocatalytic behaviour to proton reduction in acidic solutions. This property enhances crevice corrosion resistance by promoting the active-to-passive transition within the crevice, thereby inducing repassivation of active sites. The Grades-7 and -11 titanium alloys (Table 1) were specifically designed to perform as crevice corrosion-resistant alloys at elevated temperatures in concentrated chloride environments. Both the iron and nickel intermetallic compounds can catalyze the proton reduction reaction and the Grade-12 titanium was specifically designed to promote crevice repassivation and provide an inexpensive crevice corrosion resistant alternative to the Pd-containing alloys.

Compared to the Pd alloys, iron- and nickel-containing titanium materials have diminished resistance to crevice initiation, possibly because of the activity of both the iron and nickel intermetallic compounds. The small amount of iron present in commercially pure titanium can be beneficial to crevice corrosion resistance because of the electrocatalytic properties of the intermetallics formed. Precipitation of iron in titanium occurs at >0.05 wt.% iron in the metal, well below the allowable concentration of 0.2-0.3 wt.%. This small amount of iron can increase the resistance to crevice attack (Ikeda et al. 1990a, 1994; Tsujikawa and Kojima 1991) and, when combined with traces of nickel, can result in marked crevice corrosion resistance. The presence of iron also appears to enhance the coprecipitation of nickel from solution. Much of the iron and nickel concentrates in the β-phase and the intermetallics found at grain boundaries and triple points. These features may act as cathodic sites that catalyze the proton reduction reaction inside the crevice and induce repassivation, thereby limiting the extent of corrosion damage. Increasing the nickel concentration reinforces crevice repassivation. Grade-12 titanium (containing 0.7wt.%

nickel and 0.3wt.% molybdenum) was specifically designed to promote such a repassivation process and, hence, to provide an inexpensive crevice corrosion resistant alloy.

As discussed above, Grade-12 titanium resists crevice corrosion at temperatures below ~65-70°C. AC impedance results indicate a change in film structure at temperatures near 70°C. The results are consistent with the development of pores and faults in the passive layer as a result of film recrystallization. For Grade-12 titanium the metal at the base of these pores - possibly a Ti_2Ni particle - appears active whilst for Grade-16 titanium the end of the pore is inactive - possibly due to the presence of a noble metal containing particle. Grade-2 titanium has a defective film at 70°C but the pores are too resistive to interrogate by ac impedance. Clearly, the microstructural composition of the metal influences the integrity of the passive film with impurities, alloying elements and grain boundaries acting as weak points to maintaining film integrity. The chemical activity of these fault generators determines the susceptibility to crevice corrosion and the activity is determined by the material chemistry. For wisely alloyed titanium materials it is the materials properties and not the exposure environment that influence the crevice corrosion resistance. Consequently, small amounts of alloying elements such as Pd can substantially limit the degree of crevice corrosion independent of the exposure environment.

3.6 HEAT TREATMENT AND WELDING

The production of a waste container will involve heat treatments to anneal the material after fabrication, and during welding of the final closure. For many materials careful welding procedures must be followed to prevent premature corrosion failures induced by poor microstructural control in the heated zones. The dilute titanium alloys such as Grades-2 and -12 titanium are essentially single-phase materials that do not suffer from detrimental phase transformations during welding. Consequently, post-weld annealing is generally not required. Grain coarsening or refinement does not readily occur on heat treatment although prior β-phase precipitation is observed in the welded material. Since these dilute titanium alloys contain only low concentrations of impurities, the microstructures produced by welding do not generate significant impurity segregation, a process that can result in poor corrosion performance. The redistribution of iron and nickel phases can be beneficial to the crevice corrosion resistance if these elements concentrate at grain boundaries and triple points (Ikeda et al. 1990a, 1994). Measurements of the corrosion rate on artificially creviced weld zones indicate that the welded coupons corrode slightly slower than unwelded specimens but the total extent of corrosion is not significantly different. The maximum penetration depth increases with distance from the weld metal through the heat affected zone into the base metal (Shoesmith et al. 1995b). The effect of heat treatment and welding on the crevice corrosion performance of titanium will be either beneficial, or of no significance.

3.7 IRRADIATION

The evaluation of a candidate nuclear waste container material should include an assessment of radiation effects on corrosion. Experiments have been performed in low gamma-radiation fields similar to those anticipated at the surface of a waste container. Long-term exposure to simulated disposal vault environments including an ~5 $Gy \cdot h^{-1}$ gamma-radiation field from a cooled used

CANDU® fuel bundle did not lead to increased susceptibility to crevice corrosion, or to any other form of accelerated corrosion attack (Ikeda and Clarke 1986, Ikeda et al. 1988, Ryan et al. 1994, Ikeda and McKay 1984, McKay and Ikeda 1985). Electrochemical experiments in similar radiation fields indicate a generation of stable oxidizing conditions (Ikeda 1985) but no acceleration of the crevice corrosion rate on Grade-2 titanium. The presence of radiation during the initiation of crevice corrosion appears to induce a rapid repassivation of the reaction, limiting the overall extent of damage. Introducing the radiation field to an actively propagating crevice leads to an immediate decrease in propagation rate, possibly as a result of the generation of oxidizing radicals in the crevice. However, the effect is small and propagation still continues until the oxygen is depleted. The overall influence of gamma-radiation is small, either having little influence on the overall extent of reaction, or enhancing the resistance of the material to crevice attack.

4. FACTORS DRIVING REPASSIVATION OF CREVICES ON TITANIUM

Repassivation of an active crevice on Grade-2 titanium will only occur when the oxygen concentration in the vault environment falls to a low value, i.e., all the available oxygen is consumed. If access to air were unlimited, rapid penetration could occur. However, the disposal vault environment will have a limited amount of oxygen trapped in the facility and its transport to the container surface will be restricted by the presence of the compacted clay/sand buffer layer. This barrier can decrease the diffusion coefficient of oxygen by a factor of 100. Thus, the concentration of oxygen close to a container surface will be rapidly reduced to a low value and its replenishment by transport through the buffer will be slow.

The development of a damage function based upon the maximum penetration depth achieved in a closed (fixed oxygen) environment demonstrates the relationship between the available oxygen and the damage to the metal caused by crevice corrosion. The extrapolation of this function, obtained for 100 and 150°C, shows that container penetration will not occur given the amount of oxygen trapped in a borehole for the borehole-emplacement configuration. If the full container wall thickness were available as a corrosion allowance (i.e., the container is internally supported) then a substantial titanium wall thickness will remain after all the oxygen has been consumed by crevice corrosion. This form of repassivation can be accelerated if the oxygen concentration is decreased rapidly by reaction with minerals or organic matter present in both the rock and buffer material. A similar control of the available oxygen would occur for the in-room emplacement configuration. For this case the use of larger quantities of buffer would introduce larger quantities of oxygen. However, the use of granitic, as opposed to silica, sand would correspondingly increase the oxidizable mineral content leading to oxygen consumption.

Crevice repassivation can be achieved in the presence of oxygen if: (i) the titanium contains substantial iron or nickel impurities; (ii) solution species that control propagation and induce repassivation, e.g., sulphate, are present naturally in the groundwater; or (iii) inhibitors arise from dissolution of mineral species in the rock, buffer or backfill materials. Choosing a crevice repassivating alloy such as Grade-12 or -16 titanium will ensure a limited or non-existent crevice

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corrosion period, respectively. The maximum extent of crevice corrosion on Grade-12 titanium will be limited by its inability to propagate at T<70°C. The damage caused by crevice corrosion on Grade-12 titanium is also dependent on material properties so the predictability of the attack will depend upon the uniformity, in composition and microstructure, of the manufactured material. Experience indicates a variability in materials properties that leads to some variability in repassivation behaviour. Despite this, measurements of the depth of corrosion penetration show a maximum limited to ~1 mm depth irrespective of the time of repassivation.

The palladium-containing titanium alloys resist crevice initiation. Negligible crevice propagation has been observed, probably because the catalysis of the proton reduction reaction at noble metal sites reinforces passivation, even in aggressive environments. Only small amounts of palladium are required to enhance the crevice corrosion resistance of titanium in neutral pH saline environments.

5. MODELS FOR PREDICTING THE EXTENT OF CREVICE CORROSION DAMAGE

Justifying the use of any material for the construction of a nuclear fuel waste container requires a computational model to predict the time-to-failure for the container. Assuming that mechanical and corrosion performance can be modeled independently, the corrosion failure model will predict the time required for corrosion penetration to exceed the corrosion allowance. Two independent models have been developed to predict the lifetime of a thin-walled Grade-2 titanium container. The container failure model used in the EIS case study (Johnson et al. 1994a) was based on a classical corrosion-rate type of analysis, and subsequently a damage function model was developed based on measured penetration depths (Shoesmith et al. 1995c). Both models predict that a titanium container with a 4.35 mm corrosion allowance will have a lifetime of >1000 a - well in excess of the minimum containment lifetime of 500 a.

The complete failure function, used in the vault postclosure assessment, consists of three components: failure by undetected flaws, failure by crevice corrosion and failure by hydrogen cracking. The calculation of the premature failure frequency is based on a reliability analysis of carefully inspected pressure-retaining components (Doubt 1985). The anticipated similarity in quality assurance suggests that the statistical distribution of failures caused by undetected flaws will be similar for both inspection procedures. The defective containers were assumed to fail over a 50-a period.

Crevice corrosion was assumed to cause container failure once the wall thickness decreased to 2 mm (Section 1.1 above). It was assumed that there would be sufficient oxygen in the vault to sustain crevice corrosion at a constant rate over its lifetime. The mean corrosion rate was calculated based on: (1) the temperature dependence found for crevice propagation on Grade-2 titanium, and (2) the corrosion rate determined from an immersion experiment performed under simulated disposal vault conditions that included radiation. By using an immersion test specimen to specify the base corrosion rate, the oxygen concentration was fixed at the average concentration over the duration of the experiment, a three month period. This simulated a low, but constant, oxygen concentration in the vault environment over the period of crevice corrosion.

Hydrogen cracking was assumed to be a low temperature process such that failures occurred when the temperature fell below 30°C. This failure mechanism dominates when the crevice corrosion rate has fallen to a low value. The substantial amounts of hydrogen absorbed by the material during crevice corrosion at $T > 30°C$ would then precipitate to form a brittle hydride capable of sustaining cracking in the metal (Shoesmith et al. 1997). The initiation time for cracking was assumed to be distributed over time but its propagation rate was assumed to be infinitely fast. The distribution of failure times was centered at the mean time for the containers to cool to 30°C, and spread around that time by the variability in the transition time over all the containers in a group.

The container failure model was based upon the observed Arrhenius behaviour (Ikeda et al. 1990b). The crevice corrosion rate was linked to the time-dependent temperature profiles for the containers which varied because of their geometric position in the disposal vault. The temperature profiles were simplified by dividing the containers into three groups - hot containers located in the center of the vault, cool containers around the vault periphery, and cold containers located near the corners of the vault. A detailed description of the procedure used to analyze the profiles and separate them into these groups, and the analysis to justify this simplification, is given elsewhere (Shoesmith et al. 1995b and 1995c). Briefly, the temperature profiles were averaged to produce step functions that approximated the original temperature profiles for all the containers in a group. The simplified temperature function represented the mean container temperature with an associated variability. Each group of containers was assigned a corrosion rate chosen from a normal distribution derived from the temperature distribution. This formed the basis of a probabilistic assessment of the container lifetime, the details of which are given elsewhere (Shoesmith et al. 1995b).

This model predicts that <0.1% of the containers will fail before 1000 a, and significant numbers of containers will begin to fail only after 1200 a. By 2500 a, ~60% of the containers will have failed including all the containers in the hot regions. The last containers will survive for ~6000 a. This distributes the radionuclide release over a 1200-6000 a period, during which time the radiotoxicity in the vault will have fallen substantially. The container surface temperatures will have fallen to between 25 and 60°C when the last container fails. The model did not contain an explicit oxygen concentration dependence and relied on the extrapolation of short-term data.

To address these issues an independent analysis involving the determination of a damage function was undertaken. A damage function empirically relates the amount of damage, i.e., the measured maximum penetration depth, to a critical parameter such as oxygen availability or time. Such a damage function was constructed to describe the crevice corrosion of Grade-2 titanium (Shoesmith et al. 1995c). A comparison of failure times predicted by both models clearly shows that the container failure function used in the postclosure assessment underestimates the corrosion damage during the early stages of corrosion, but overestimates the depth of penetration after long exposure times. Consequently, the container failure function predicts a shorter container lifetime than the damage function, even though the damage function is based on crevice corrosion at a constant temperature of 100°C whereas the container failure function takes into account the decay in temperature of the containers from a maximum of ~95°C.

By relating the penetration depth to oxygen consumption instead of exposure time, a single damage function can be used to represent the maximum penetration depth at both 150 and 100°C. Since the maximum amount of oxygen that could be trapped in the disposal vault can be estimated (Shoesmith et al. 1995c) the maximum penetration expected on a waste container can be predicted. This analysis cannot be used to predict a container failure rate, but it shows that there will be insufficient oxygen in the disposal vault for crevice corrosion failure of the container.

Although neither the container failure function nor the damage function includes an explicit oxygen dependence, the damage function analysis provides a defensible upper bound on the effect of trapped oxygen on container performance. This is an important consideration in the failure analysis because the time-dependent oxygen concentration in the disposal environment is difficult to determine. Both of the models assume instantaneous saturation of the borehole (and buffer) to ensure corrosion initiates immediately upon emplacement. As discussed in Section 1.2, this is unlikely and crevice corrosion could be avoided altogether by a period of undersaturation lasting ~200 a, the time required for the temperature of all containers to fall below the critical crevice initiation temperature of ~70°C (providing the unsaturated conditions do not substantially alter the thermal behaviour of the buffer). For this condition a container failure model based on crevice corrosion would be inappropriate and a long-term failure model based on uniform corrosion conditions would be required (Shoesmith et al. 1995a). The container failure models described are amenable to further improvements which include an oxygen concentration dependence, provided: (1) the appropriate experimental data are available; (2) oxygen mass transport modeling is available; and (3) borehole saturation modelling is developed.

6. FUTURE WORK REQUIRED

If the predictions of container lifetimes are to be improved, then a number of further measurements are required to establish the limits of crevice corrosion on Grades-2, -12 and -16 titanium. The databases for the damage functions of these materials need to be improved, and the determination of the duration of the crevice corrosion period must be established. For each material, there is a requirement to determine the factors that limit the extent of crevice corrosion damage. Specific requirements for each material are outlined below.

Coupling the corrosion rate at different temperatures and the critical oxygen concentrations with mass transport calculations will provide a prediction of the crevice corrosion period. The damage function can then predict the maximum extent of crevice corrosion damage. Combining this maximum crevice corrosion with that expected from subsequent uniform passive corrosion will provide the lifetime prediction for Grade-2 titanium containers (Shoesmith et al. 1995a).

Grade-12 titanium has better crevice corrosion resistance than Grade-2 titanium but crevice penetration is more localized. The following additional information is needed:

(1) A damage function (maximum depth of penetration) is required for various temperatures and complex groundwaters.

(2) The critical oxygen concentration for crevice initiation and repassivation is required. This is required to established the duration of the potential crevice corrosion period.

(3) The properties of the passive film must be established. We have shown that the properties of the film influence the initiation/repassivation behaviour of Grade-12 titanium and that the underlying microstructure influences the film properties. Establishing the critical properties of the film - such as recrystallization temperature - is critical to determining the protective nature of the film.

Grade-16 titanium has excellent crevice corrosion resistance. However, at this time, the effect of hydrogen content on its behaviour is not known and therefore all three materials should be maintained as options. To justify the long term predictions of crevice corrosion resistance, it is important to understand the behaviour of the passive film on Grade-16 titanium. Determining properties such as the passive film recrystallization temperature is important to justify that localized corrosion cannot occur.

The Grade-2 titanium damage function must be improved before this modeling approach can be fully justified in modeling container failure. A more extensive database of crevice penetration depths at different temperatures is required, and additional information is needed to justify reasoned arguments that the damage function is a conservative estimate of the total possible damage. The required experimental data include the following:

(1) the critical oxygen concentration below which crevice repassivation is inevitable;

(2) mass transport calculations to determine the flux of oxygen to the container;

(3) a measure of the steady-state corrosion rate and associated crevice penetration depths with temperature.

The work to date has established that, on the basis of a crevice corrosion model, container lifetimes will exceed the minimum 500-a criterion. Much longer lifetimes can be achieved under passive corrosion conditions (Shoesmith et al. 1995a). However, establishing that passive conditions can be maintained following minimal crevice corrosion damage will require both experimental work and modeling to determine the influence of mass transport limitations and unsaturated buffer/backfill conditions on crevice corrosion.

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