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Review of the Expected Behaviour of Alpha Titanium Alloys Under Yucca Mountain Conditions

Examen du comportement prévu des alliages de titane alpha dans les conditions du mont Yucca

D.W. Shoesmith

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REVIEW OF THE EXPECTED BEHAVIOUR OF ALPHA TITANIUM ALLOYS UNDER YUCCA MOUNTAIN CONDITIONS

D.W. Shoesmith*

REPORT PREPARED FOR THE U.S. DEPARTMENT OF ENERGY,
YUCCA MOUNTAIN SITE, CHARACTERISATION OFFICE
UNDER AECL TECHNOLOGIES INC.
CONTRACT # DE-AC08-95-NV11784

*D.W. Shoesmith
Department of Chemistry
University of Western Ontario
London, Ontario N6A 5B7

Engineered Barriers and Analysis Branch
Whiteshell Laboratories
Pinawa, Manitoba R0E 1L0
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EXAMEN DU COMPORTEMENT PRÉVU DES ALLIAGES DE TITANE ALPHA DANS LES CONDITIONS DU MONT YUCCA

D.W. Shoesmith*

RAPPORT RÉDIGÉ POUR L'U.S. DEPARTMENT OF ENERGY,
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RÉSUMÉ

On a examiné l'utilisation des alliages de titane dans deux types d'emballages de déchets différents dans les conditions prévues au dépôt des déchets nucléaires du mont Yucca. Dans le premier modèle, ces alliages sont considérés comme un des trois matériaux barrières intégrés dans le type d'emballage des déchets et potentiellement en contact galvanique avec les deux autres matériaux d'emballage des déchets, l'acier inoxydable 316L et l'alliage 22. Dans le deuxième modèle, l'alliage Ti est considéré comme un écran d'égouttement placé, sans le toucher, par-dessus un emballage de déchets à paroi double fabriqué à partir des deux autres matériaux.

Les processus de défaillance possibles, la corrosion caverneuse, le piquage et la fissuration due à l'hydrogène ont été examinés dans le cas des alliages de titane candidats (Ti 12, Ti 16 et Ti 7). Le piquage et la corrosion caverneuse sont des possibilités très éloignées dans ces conditions. Dans le cas du Ti 12, il est possible qu'il y ait un peu de corrosion caverneuse, mais la repassivation se produit avant qu'il n'y ait des dommages importants. Quand le Ti est pris en compte comme faisant partie intégrante de l'emballage des déchets à paroi triple, l'absorption d'hydrogène menant à la fissuration due à l'hydrogène, à l'intérieur d'une crevasse acidifiée, mais passive, constitue le mécanisme de défaillance le plus vraisemblable. Quand on utilise l'alliage Ti sous la forme d'un écran d'égouttement, ce que l'on craint le plus c'est l'absorption d'hydrogène dans des conditions alcalines potentielles.

On a démontré que le Ti 12 et le Ti 16 toléraient des quantités importantes d'hydrogène (~400 $\mu g \cdot g^{-1}$ pour Ti 12, et > 1000 $\mu g \cdot g^{-1}$ pour Ti 16) avant que l'on observe des effets sur la ténacité à la rupture des matériaux. Le taux d'absorption à une teneur en hydrogène dépassant ces valeurs sera la caractéristique clé pour déterminer si, ou quand, le matériau devient sensible à la fissuration. Une fois que l'on a rempli cette condition, la rupture dépendra de la résistance et de l'emplacement des contraintes à l'intérieur de la structure.

Pour que le Ti absorbe l'hydrogène, il est inévitablement nécessaire de soumettre le matériau à une polarisation cathodique, soit en l'associant à une matière plus active ou en appliquant la protection galvanique. L'absorption se fait quand le TiO_2 passif est rendu perméable à l'hydrogène en provoquant cathodiquement des transformations redox dans l'oxyde ($Ti^{4+} \rightarrow Ti^{3+}$). Toutefois, la présence de particules intermétalliques (Ti_2Ni dans le Ti 12, Ti_xPd dans le Ti 7/Ti 16) pourrait permettre l'absorption

d'hydrogène à des polarisations cathodiques inférieures, du fait que ces particules pourraient jouer le rôle de «fenêtres» d'absorption d'hydrogène dans l'oxyde. On a démontré que cela se produisait pour Ti 12, mais pas pour le Ti 16. Au contraire, il semble que les particules intermétalliques présentes dans le Ti 16 empêchent l'absorption d'hydrogène.

Si la défaillance du Ti par absorption d'hydrogène entraînant la fissuration due à l'hydrogène doit se produire, alors le titane cathodique doit se coupler à une anode disponible. Dans le cas du Ti 12, des particules intermétalliques de Ti_2Ni sont corrodables et leur corrosion anodique pourrait se coupler à l'absorption d'hydrogène par la matrice d'alliage. Dans le cas du Ti 16 les particules intermétalliques sont inertes et donc ne semblent pas représenter une voie faisable pour l'absorption d'hydrogène. Une deuxième possibilité est que, en présence de F^-, la dissolution passive améliorée pourrait se coupler à l'absorption d'hydrogène. C'est une possibilité plus vraisemblable dans des conditions acides d'une crevasse métallique mixte que dans les conditions plus alcalines prévues sur l'écran d'égouttement. L'évidence tirée des études dentaires et des études sur les épurateurs des gaz d'échappement indique que ceci est peu probable, spécialement dans le cas des alliages contenant du Pd. Toutefois, cette évidence n'est pas totalement concluante. D'autres anions, SO_4^{2-} et HCO_3^-, et l'espèce, la silice, que l'on s'attend à trouver dans de bonnes quantités dans les eaux souterraines concentrées du mont Yucca, risquent fort de contrebalancer toute agressivité du F^-. Dans les solutions alcalines, F^- ne semble pas être capable d'améliorer le processus de corrosion passive.

La possibilité finale qui pourrait déboucher sur l'absorption d'hydrogène par les alliages de Ti est leur couplage aux autres matières d'emballage des déchets, c.-à-d. alliage 22 et acier inoxydable 316L. En fait, ceci n'est réalisable que si le Ti est intégré au type d'emballage des déchets à paroi triple. Un couplage actif entre un alliage de Ti et l'alliage 22 est très peu probable, du fait que tous les deux sont des matières passives sur lesquelles la corrosion active est très difficile à amorcer. Un couple comprenant l'acier inoxydable 316L et un alliage de Ti pourrait être actif s'il y avait une perte de passivité sur l'acier. Ceci reste une possibilité jusqu'à ce que les essais prouvent le contraire. En se fondant sur ces études, l'ordre de préférence de ces alliages en tant que matériaux pour les emballages de déchets serait

$$\text{Ti } 16 \geq \text{Ti } 7 >> \text{Ti } 12.$$

Toutefois, avant de pouvoir recommander avec certitude que l'on choisisse le Ti 16 de préférence au Ti 7, on doit mieux comprendre le comportement déconcertant actuel des particules intermétalliques dans ce matériau.

*D.W. Shoesmith
Département de chimie
University of Western Ontario
London (Ontario) N6A 5B7

Barrières ouvragées et Analyse
Laboratoires de Whiteshell
Pinawa (Manitoba) R0E 1L0
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ABSTRACT

The use of titanium alloys in two different waste package designs has been reviewed under the conditions anticipated in the Yucca Mountain nuclear waste repository. In the first design, they are considered as one of three barrier materials incorporated into the waste package design, and potentially in galvanic contact with the other two waste package materials, 316L stainless steel and Alloy-22. In the second design the Ti alloy is considered as a drip shield placed over, and not in contact with, a dual wall waste package fabricated from the other two materials.

The possible failure processes, crevice corrosion, pitting and hydrogen-induced cracking (HIC) have been reviewed for the candidate titanium alloys (Ti-12, Ti-16 and Ti-7). Both pitting and crevice corrosion are very remote possibilities under these conditions. For Ti-12, a limited amount of crevice corrosion is possible but repassivation will occur before substantial damage is sustained. When Ti is considered as part of the triple wall waste package, hydrogen absorption leading to HIC, within an acidified but passive crevice, is the most likely failure mechanism. When the Ti alloy is utilized in the form of a drip shield then hydrogen absorption under potentially alkaline conditions is the major fear.

Both Ti-12 and Ti-16 have been shown capable of tolerating substantial amounts of hydrogen (~400 $\mu g \cdot g^{-1}$ for Ti-12, and > 1000 $\mu g \cdot g^{-1}$ for Ti-16) before any effect on the materials fracture toughness is observed. The rate of absorption to a hydrogen content which exceeds these values will be the key feature determining if, or when, the material becomes susceptible to cracking. Once this condition is achieved, whether or not failure occurs will depend on the strength and location of stresses within the structure.

For Ti to absorb hydrogen it is inevitably necessary to subject the material to cathodic polarization, either by coupling to a more active material or by the application of galvanic protection. Absorption occurs when the passive TiO_2 is rendered permeable to hydrogen by cathodically inducing redox transformations in the oxide ($Ti^{4+} \rightarrow Ti^{3+}$). However, the presence of intermetallic particles (Ti_2Ni in Ti-12, Ti_xPd in Ti-7/Ti-16) could allow hydrogen absorption at lower cathodic polarizations, since these particles could act as hydrogen absorption "windows" in the oxide. This has been shown to occur for Ti-12, but does not appear to occur for Ti-16. On the contrary, there is speculative evidence to suggest that the intermetallics present in Ti-16 inhibit hydrogen absorption.

If failure of Ti by hydrogen absorption leading to HIC is to occur then the cathodic titanium must couple to an available anode. For Ti-12, the Ti_2Ni intermetallics are corrodable and their anodic corrosion could couple to hydrogen absorption by the alloy matrix. For Ti-16 the intermetallics are inert and thus do not appear to be a feasible pathway for hydrogen absorption. A second possibility is that in the presence of F^- enhanced passive dissolution could couple to hydrogen absorption. This is a more likely possibility under acidic conditions in a mixed metal crevice than it is for the more alkaline conditions anticipated on the drip shield. The evidence from dental and flue gas scrubber studies suggest this is unlikely, especially with the Pd-containing alloys. The evidence, however, is not totally conclusive. Other anions, SO_4^{2-} and HCO_3^-, and the species, silica, expected to be present in copious amounts in concentrated groundwaters at Yucca Mountain, are very likely to counterbalance any aggressiveness of F^-. In alkaline solutions, F^- does not appear able to enhance the passive corrosion process.

The final possibility that could lead to hydrogen absorption by Ti alloys is their coupling to other waste package materials; i.e. Alloy-22 and 316L stainless steel. Clearly, this is only achievable if Ti is incorporated into the triple wall waste package design. An active couple between a Ti alloy and Alloy-22 is very unlikely, since both are passive materials on which active corrosion is extremely difficult to activate. A couple involving 316L and a Ti alloy could be active if there was a loss of passivity on the steel. This remains a possibility until tests prove otherwise.
Based on these studies the order of preference of these alloys as materials for waste packages would be

$$\text{Ti-16} \geq \text{Ti-7} \gg \text{Ti-12}.$$

However, before a confident recommendation that Ti-16 be chosen over Ti-7, a better understanding of the presently baffling behaviour of the intermetallic particles in this material is required.

*D.W. Shoesmith
Department of Chemistry
University of Western Ontario
London, Ontario N6A 5B7

Engineered Barriers and Analysis Branch
Whiteshell Laboratories
Pinawa, Manitoba R0E 1L0
2000 March

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1. INTRODUCTION

Advanced waste package designs are under consideration for use in the Yucca Mountain Repository. The present reference design employs a dual wall arrangement, in which a 2 cm-thick nickel alloy inner barrier is encapsulated within a 10-cm thick mild steel outer barrier. The pros and cons of this design have been discussed in detail (Van Konynenburg 1998) elsewhere and a case for its usage presented (US Department of Energy 1998).

The major corrosion issue with this reference design is the possible formation of hot, saline ferric ion solutions in contact with the inner barrier alloy (Alloy-22). The source of this environment is the corrosion of the outer barrier carbon steel. Besides potentially producing a corrosive environment on the inner barrier corrosion resistant alloy it has proven difficult to justify that the carbon steel outer barrier itself will provide long term protection of the inner barrier from corrosion. While many of these reservations are unduly pessimistic, it is judicious to consider alternative materials which avoid these uncertainties.

With these reservations in mind, it has been proposed that the carbon steel be replaced by a second corrosion resistant material which will not suffer any common mode corrosion failure with Alloy-22. While final decisions on package design remain to be made, two designs have recently been proposed for evaluation. One involves a triple wall container in which both Alloy-22 and a Ti alloy would be employed as corrosion barriers along with a supporting structure fabricated from 316L stainless steel. The second design would use a Ti alloy drip shield over a waste package fabricated from Alloy-22 and 316L.

The purpose of this report is to review the corrosion performance of possible titanium alloys for this application. The alloys under consideration are the Pd-containing alloys Grades-7 and -16, and, to a lesser degree, the nickel/molybdenum containing Grade-12 alloy. The ASTM nominal maximum compositions (expressed as weight %) for these alloys are given in Table 1. The commercial purity Grade-2 alloy composition is given for comparison, and its corrosion behaviour is often used throughout this report as a reference point against which to discuss the corrosion behaviour of the other alloys.

The review will concentrate on potential corrosion processes possible in aqueous environments at Yucca Mountain. A brief review of passive oxide (TiO_2) properties, and how they could be affected by the key environmental variables of redox potential, pH and temperature will be given. Then the key corrosion processes which could occur will be addressed individually. Finally, the expected corrosion performance of these alloys under the specific environmental conditions anticipated at Yucca Mountain will be considered. In the main body of the report the discussion concentrates on the corrosion performance of the triple wall container. Since the design utilizing a Ti alloy as a drip shield was only proposed for consideration after this report was initially completed, discussion of the corrosion performance anticipated with this arrangement is given in an appendix.

TABLE 1

ASTM NOMINAL COMPOSITIONS (wt.%) FOR VARIOUS GRADES OF TITANIUM

Grade	N	C	H	Fe	O	Mo	Ni	Pd
2	0.03	0.10	0.015	0.30	0.25			
12	0.03	0.10	0.015	0.30	0.25	0.3	0.8	
7	0.03	0.10	0.015	0.30	0.25			0.2
16	0.03	0.10	0.01	0.30	0.25			0.05

2. PROPERTIES OF PASSIVE FILMS ON TITANIUM

It is universally accepted that the protectiveness of the passive oxide film is the key feature which confers on titanium its ability to resist corrosion. Here, a number of pertinent oxide properties, and how they are likely to be affected by environmental variables, are discussed. A more extensive discussion has been presented elsewhere (Shoesmith and Ikeda 1997).

Figure 1 summarizes the changes expected in passive oxide properties as a function of potential, pH and temperature. Apart from specific features of anticipated groundwater composition, these three parameters are the most significant under waste repository conditions.

The potential experienced by the titanium surface will be dictated by the redox conditions of the exposure environment. These will generally be oxidizing due to the ubiquitous presence of air, but could be affected by the formation of galvanic couples between titanium and the other waste package materials. Reducing conditions could be established within occluded sites to which the access of oxygen is transport limited.

The pH, while generally anticipated to be neutral to slightly alkaline could be influenced by minor corrosion processes within occluded sites such as crevices.

The temperature within the waste repository could range from well over 100°C to eventually ambient. From the perspective of aqueous corrosion only temperatures which allow the establishment of aqueous conditions are of significance. For higher temperatures, the unsealed nature of the waste vault will reduce local humidities to low, and hence innocuous, levels. Taking into account the anticipated electrolyte concentration processes possible due to periodic wetting and drying of the waste package surface, a maximum temperature for aqueous conditions of ~125°C appears feasible (G. Gordon, personal communication).

2.1 EFFECT OF POTENTIAL

The passive oxide grown under open-circuit conditions at room temperature may be amorphous or crystalline depending on the conditions of growth. However, the maintenance of an amorphous oxide structure over extremely long exposure times seems unlikely. The thickness of the oxide and its degree of crystalline order may vary spatially (Kuldelka et al. 1995), 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 and a decrease in the number density of defects. Amorphous films recrystallize to anatase over the potential range 4 to ~7 V (vs SCE[1]) and cracks and faults begin to appear in the oxide (Shibata and Zhu 1995). 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 (≥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. This pitting process is specific to Br^- and not observed in Cl^- solutions. For high anodic potentials, in the region of 8 to 9 V, the breakdown of the film leads to recrystallization and a more rapid rate of thickening of the film with potential than observed at lower potentials. Potentials this positive are unattainable under natural corrosion conditions.

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 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 amount of hydrogen absorbed suggest a potential threshold of ~-0.6 V above which no absorption occurs.

2.2 EFFECT OF TEMPERATURE

The effect of temperature on films grown either electrochemically or under natural corrosion conditions 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 temperature in NaBr solutions shows this absorption of water improves the passivity of the oxide as indicated by a marked increase in pitting potential (Shibata and Zhu 1994).

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[1] SCE, Standard Calumet Electrode

2.3 EFFECT OF pH

The pH has no effect on oxide stability for $E \geq -0.3$ 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 (Kelly 1979). At room temperature in chloride solutions, a pH between 1 and 0 is required before active conditions can be established (Watanabe et al. 1989). For a temperature of 70°C, a pH < 1 is required. For natural corrosion conditions, the dissolution of the oxide film in acidic solutions is slow (~20 μm/y at pH < 0 and 45°C) and in solutions of pH > 1, extremely slow (~2 μm/y at pH~1 and 45°C) (Blackwood et al. 1988). Cathodic polarization in acidic solutions leads to the reductive dissolution of the oxide (Ti^{IV} (oxide) $\rightarrow$ Ti^{III} (solution)) (Ohtsuka et al. 1987), a process which is accompanied by the absorption of hydrogen into the oxide.

To avoid the two processes most likely to lead to localized corrosion, crevice corrosion and hydrogen-induced cracking (HIC), practical industrial 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 be < 3 or > 12, or the potential at the surface must be < -0.7 V (Schutz and Thomas 1987). Further consideration of these guidelines will be included when discussing the corrosion behaviour of the individual alloys.

3. CRITICAL CORROSION PROCESSES

If Ti alloys are to fail rapidly due to corrosion then the most likely processes are crevice corrosion, pitting, and hydrogen induced cracking (HIC) under either aqueous or vapour phase conditions. Processes such as microbially induced corrosion and radiolytically-induced corrosion are extremely unlikely and have been considered in detail elsewhere (Shoesmith and Ikeda 1997, Shoesmith and King 1999). The possibility of direct hydrogen absorption leading to HIC due to radiolysis effects is considered briefly below.

3.1 VAPOUR PHASE CORROSION

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- and sulphur-bearing gases below 300°C, and Ti is the preferred metallic material for handling wet Cl_2 and Br_2 environments. The resistance of Ti alloys to rural, marine and urban atmospheric environments has been documented (Covington and Schutz 1981). Titanium alloys are widely used in H_2-containing environments, and in the presence of traces of moisture or O_2, the surface oxide film is a highly effective barrier to hydrogen absorption (Cotton 1970, Covington 1979).

Atmospheric corrosion has been studied at elevated temperatures, but not at temperatures below 200°C. Moroishi and Shida (1980) studied the oxidation of commercially pure Ti in air saturated with steam at 0.1Mpa (1 atmosphere) for 24 to 101 days at temperatures between 400 and 550°C. The oxidation rate varied from 2.6 to 45 mm/year over that range and breakaway corrosion was only observed at 550°C. Extrapolation of their data to lower temperatures would suggest corrosion rates of ~5 μm/year at 100°C and <1 μm/year at 25°C. These extrapolated estimates are much higher (orders of magnitude) than those summarized by Schutz and Thomas (1987) and Covington and Schutz (1981).

The corrosion performance of Ti and Ti alloys has been investigated in contact with clay and moist clay atmospheres. While the proposed backfill to be used at Yucca Mountain is unlikely to be clay, these studies represent the closest simulation of anticipated repository conditions presently available. The majority of these studies were conducted on either commercially pure Ti (equivalent to Ti-2) or Ti-7. No measurable differences in performance were observed between the two materials, although Ti-7 was more universally tested than the commercially pure Ti (DeBruyn et al. 1990). Tests were performed in direct contact with clay at both 90°C and 17°C for exposure periods up to 6 years. No significant weight change was observed, and optical microscopy and metallography showed no discernible 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 and 170°C) no evidence for corrosion damage was found even in the presence of a radiation field (10^3Gy/h ≡ 10^5R/h).

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 $\mu g.g^{-1}$) and a flow of 250 L/h 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 was tested. After 49 months at 50°C in the corrosion chamber only the Ti alloys (Ti-2, Ti6Al4V, Ti5Al2Sn) showed no evidence of pitting, and, despite the formation of deposits, there was no observable crevice (under deposit) corrosion. After 3 years 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 corrosion.

If humid vapour conditions are established sufficiently rapidly, then the possibility for the radiolytic production of HNO_3 and H_2 exists. While a feasible scenario, this will not lead to significant corrosion of Ti for a number of reasons. The predominant reason is that by the time humid vapour conditions can be established (after several thousand years) radiation fields will have decayed to innocuous levels. However, even if this were not the case, the resistance of Ti and Ti alloys to radiolytically-induced corrosion is extremely good, and, at worst, only a minor thickening of the passive oxide would be expected (Shoesmith and King 1999). The production of an acid such as HNO_3 would have a passivating effect, the resistance of Ti to corrosion in oxidizing acids having been well-documented (Schutz and Thomas 1987). The direct absorption of hydrogen produced radiolytically requires much higher temperatures and dose rates than those which will prevail when humid conditions exist at Yucca Mountain. Hydrogen absorption has only been observed (under basaltic conditions) at 250°C for gamma dose rates > 10^2 Gy/h (≡ 10^4 R/h) (Shoesmith and King 1999).

Based on these studies the possibility of Ti corrosion under vapour phase conditions at Yucca Mountain seems either remote, or an easily avoidable possibility. If placed on the outside of the waste package, Ti should not be exposed to the high temperature pressurized steam environment that could lead to hydrogen absorption. Yucca Mountain is an unsealed site and very low drift humidities are expected for waste package temperatures over 100°C. Only when the temperature drops below 100°C would saturated vapour conditions be anticipated, and these temperatures would be too low for water decomposition leading to hydrogen absorption to occur.

If titanium were the inner barrier material, then a number of environmental features could make the material susceptible to hydrogen absorption. The temperatures would initially be well above 200°C and any residual water within the package could produce a pressurized steam environment. This combination, coupled with high gamma radiation fields within the waste package, could cause hydrogen absorption. The evidence from studies in aqueous solutions show that hydrogen absorption can occur for gamma dose rates $> 10^2$ Gy/h at these temperatures (Westerman 1990). Absorption occurred more readily for Ti-12 than for Ti-2. This problem would seem easily avoidable by either careful drying of the waste form prior to sealing the waste package or by the addition to the waste package of relatively small amounts of water absorbing materials.

3.2 CREVICE CORROSION

The alloying additions to Ti-12, Ti-16 and Ti-7 are deliberately made to enhance their crevice corrosion resistance (Schutz 1988). The evidence to support the conclusion that they perform admirably in this function is extensive and well documented (Schutz 1988). Figure 2 shows critical crevice temperatures for Ti-12, Ti-16 and Ti-7, and the closely related Ti-Ru alloy, determined in a number of aggressive acidic and extremely oxidizing chloride environments. While in some cases Ti-12 may suffer crevice corrosion at temperatures as low as 70°C, both the Pd-containing alloys and the Ti-Ru alloy show no corrosion for $T < 200°C$, even in 10% $Fe^{III}Cl_3$ solution at pH = 2. The Ti-Ru alloy is similarly resistant to this form of corrosion (Schutz 1996). Critical crevice temperatures for Ti-2 are also included in Figure 2. The results of a comparison of the crevice corrosion resistance of these alloys, based on the immersion of a number of specimens in various aggressive environments, is given in Table 2.

A closer examination of the crevice corrosion behaviour of Ti-2, Ti-12 and Ti-16, using a galvanic coupling technique (Ikeda et al. 1989), confirms that the crevice corrosion resistance of these alloys improves according to the sequence

$$\text{Ti-2} \ll \text{Ti-12} < \text{Ti-16}.$$

Figure 3 shows values of the coupled crevice current (I_c) and potential (E_c) recorded in 0.27 mol·L^{-1} NaCl at 150°C (Ti-2 and Ti-12) or 100°C (Ti-16) (Shoesmith et al. 1995a). It is clear that the crevice propagation rate (proportional to I_c) and the extent (Q_c, equal to the area under the I_c-t curve) of crevice propagation decrease by many orders of magnitude from Ti-2 to Ti-12 and Ti-16. The distinctly different behaviours observed for the Ti-2 materials reflect the diverse properties of materials that differ in the amount and distribution of impurities, particularly iron (Ikeda et al. 1990, 1994). The shift in E_c to more positive values as I_c approaches 0 is a clear indication that crevice repassivation has occurred. For Ti-16 crevice

propagation is not observed, although a small number of attempts to initiate crevice corrosion were observed, Figure 3D.

TABLE 2

CREVICE CORROSION TEST DATA FOR Pd-CONTAINING TITANIUM ALLOYS IN ACIDIC OXIDIZING NaCl BRINES

(30 Days Exposure; Schutz and Xiao 1993)

Test Environment	Alloy	Crevice Attack Frequency	Comments
20% NaCl; pH = 2; 260°C	Ti-16	0/12	No attack
(naturally aerated)	Ti-7	0/12	No attack
20% NaCl; pH = 2; 90°C	Ti-16	0/12	No attack
(Cl_2 saturated)	Ti-7	0/12	No attack
20% NaCl; pH = 1; 90°C	Ti-2	12/12	Severe attack
(Cl_2 saturated)	Ti-16	0/12	No attack
	Ti-7	0/12	No attack
Boiling 10% $FeCl_3$;	Ti-2	12/12	Severe attack
pH = 1.0 to 0.3; 102°C	Ti-16	0/12	No attack
	Ti-7	0/12	No attack

The results of these electrochemical experiments are confirmed by weight change measurements, Figure 4 (Bailey et al. 1996), shown here as a function of chloride concentration at 150°C. No data for Ti-16 are shown since no weight change was observed on this material. It should be noted that, for Ti-12, the extent of crevice propagation (Figure 4) is severely limited by relatively rapid repassivation (Figure 3). This limitation on the extent of crevice propagation on Ti-12 was demonstrated to occur even in extremely aggressive Mg^{2+}-containing brines at 150°C (Westerman 1990). The unexpected dependence of weight change on chloride concentration (Cl^-) has been addressed elsewhere (Bailey et al. 1996).

It is generally accepted that the function of the alloying additions (Ni in Ti-12, Pd in Ti-16 and Ru in Ti-Ru) is to supply cathodic sites within the creviced area which catalyze proton reduction in the reducing acidic environment existing at actively propagating sites. This catalysis of proton reduction pushes the crevice potential into the passive region for titanium thereby forcing it to repassivate (Figure 5). While the general nature of the repassivation process is understood, the chemical/electrochemical details are not so well defined.

The most commonly accepted explanation for both the Ni/Mo-containing Ti-12 and the Pd-containing Ti-7 and Ti-16 is that corrosion of the alloy in the acidic crevice environment leads to the release of Ni^{2+} or Pd^{2+} which are then subsequently redeposits to produce Ni or Pd sites which act as proton reduction catalysts (Cotton 1967, Satoh et al. 1987, Sedriks et al. 1972, Hall et al. 1985, Schutz and Xiao 1993, Kitayama et al. 1990, McKay 1987). Figure 6A attempts to illustrate this mechanism schematically.

For Ti-12, the alternative opinion is that the Ni is localized in Ti_2Ni intermetallics which act as cathodes galvanically-coupled to the surrounding Ti α-grains (Glass 1983, Kido and Tsujikawa 1989) (Figure 6B). While the evidence for the presence of Ni^{2+} in solution during passive corrosion in strong acidic solutions (to simulate the crevice environment) is good, that for dissolved Pd^{2+} is marginal. Cotton (1967) found only ~0.9 $\mu g \cdot g^{-1}$ of dissolved Pd for Ti-7 corroding in boiling H_2SO_4. A similar redeposition mechanism to produce noble metal cathodes has been claimed for Ti-Ru (Van der Lingen and de Villiers Steyn 1994). Again, however, the amount of dissolved Ru found in solution (~0.4 $\mu g \cdot g^{-1}$) after corrosion in strong acids (10% H_2SO_4, 5% HCl) (Sedriks 1975) is marginal.

Although no real evidence is available to prove the point, it is tempting to hypothesize that Ti-12 and, to a lesser degree Ti-2 with a high Fe content, may be repassivated by a process involving dissolution of Fe^{2+} and Ni^{2+} followed by their redeposition (Figure 6A), whereas Ti-7 and Ti-16 repassivate by the galvanic coupling of intermetallic precipitates to the titanium matrix, (Figure 6B). The former process might be expected to be less efficient than the latter, thereby accounting for the limited propagation of crevice corrosion on Ti-12 and Ti-2 (high Fe).

For Pd-containing alloys there is the additional possibility that the alloying element leads to the anodic ennoblement of the alloy as a consequence of either metal dissolution or oxide growth. In both cases the preferential oxidation of Ti to produce either soluble Ti^{3+}/Ti^{4+} or TiO_2, would lead to enrichment of Pd in the surface of the alloy and, hence to its ennoblement (Figure 7).

The analytical evidence for the accumulation of Pd in the surface of Pd-containing alloys after corrosion in acid solutions is indisputable (Hubler and McCafferty 1980). Whether this is due to the redeposition of dissolved Pd^{2+} or the accumulation of Pd or Pd-containing particles after the preferential dissolution of Ti (Hubler and McCafferty 1980, Armstrong et al. 1973) is not proven. The function of the alloying element in reinforcing passivity within crevices is open to debate, and in the final analysis may not be important since active crevice corrosion is not expected. However, whether or not the alloying elements are present in α-phase solid solution, β-phase solid solution and/or intermetallic precipitates could have a significant influence on the ability of the alloy to absorb hydrogen when exposed to acidic conditions and/or galvanically coupled to another more easily corrodable material. This possibility is discussed in detail below.

3.3 PITTING

The pitting of titanium has been studied in some detail (Posey and Bohlmann 1967, Koizumi and Furuya 1973) and a review has been recently written (Shoesmith and Ikeda 1997). Commercially pure titanium (Ti-2) is extremely resistant to pitting in keeping with the excellent properties of the passive TiO_2 film under oxidizing conditions (Figure 1). Commonly, pitting potentials at room temperature are in excess of 7 V, and even for temperatures greater than 150°C are in the region of 2 V.

The fear on adding alloying elements is that the formation of intermetallic precipitates will provide sites for pit initiation, or that the stabilization of an α/β-alloy phase structure could lead to inhomogeneities in the passive film which could render it susceptible to pitting breakdown at much lower potentials. Thus the pitting potentials of Al/V containing alloys of titanium are often as low as 2 V at low temperatures and ≤ 1 V for temperatures > 100°C (Posey and Bohlmann 1967). However, these authors showed that the addition of the alloying elements present in Ti-12 (Ni, Mo) and Ti-7/Ti-16 (Pd) did not adversely affect the pitting potential of titanium. These observations, and also the influence of the common titanium impurity Fe, are summarized in Figure 8. The pitting potential is shown to be normally distributed around a conservatively low mean value of ~7 V with a σ value taken to be ~1 V (Shibata and Zhu 1994). Also indicated with a horizontal arrow is the expected small influence of chloride concentration. This figure was constructed for a temperature of ~100°C, and pitting potentials would be expected to be even higher at lower temperatures (Posey and Bohlmann 1967). The range of corrosion potentials achievable under waste repository (vault) conditions is much less than the pitting potential values and one can be confident in claiming that pitting of Ti-12, Ti-16 or Ti-7 will not occur under waste repository conditions.

3.4 HYDROGEN-INDUCED CRACKING (HIC)

It is clear from the properties of the passive film on Ti (Figure 1), that cathodic polarization leading to hydrogen absorption and eventually HIC is a much more probable failure process than pitting. Whether or not failure by this process is feasible will depend on the hydrogen content required to degrade the fracture toughness of the material, the ease of absorption of this amount of hydrogen, and whether the environment can polarize the titanium to a potential sufficiently negative for hydrogen absorption.

It has been demonstrated by Sorensen and coworkers (Sorensen 1990) that the alloy Ti-12 requires a hydrogen content of > 500 $\mu g \cdot g^{-1}$ before any measurable loss of ductility occurs. Using the slow strain rate technique on precracked compact tension specimens precharged with known amounts of hydrogen, Clarke et al. (1994, 1995) showed that the fracture toughness of both Ti-2 and Ti-12 is not significantly affected until their hydrogen contents exceed a critical value (H_c). An example of the data obtained, expressed as a plot of stress intensity factor as a function of hydrogen concentration, is shown in Figure 9. The as-received materials, containing 20 to 50 $\mu g \cdot g^{-1}$ of hydrogen, are very tough and under high stress, fail by ductile overload. This ductile tearing is also observed during slow crack growth for both materials. The value of H_c is the hydrogen concentration above which slow crack growth is no longer observed and only fast crack growth occurs. Extensive discussions of such data are available elsewhere (Shoesmith et al. 1997).

A generalized form of such a plot is shown in Figure 10, illustrating how they can be used to identify the critical hydrogen content (H_c) above which the fracture toughness is affected and one cannot then be sure these alloys will not fail by fast crack growth. Based on such measurements, values of H_c of 500 to 800 $\mu g \cdot g^{-1}$ (Ti-2) and 400 to 600 $\mu g \cdot g^{-1}$ (Ti-12) have been determined. More recent measurements (Ikeda, unpublished data) show that H_c for Ti-16 is at least 1000 $\mu g \cdot g^{-1}$ and may be much greater.

To assume fast crack growth is inevitable once H_c is attained is a conservative assumption. Implicit in this assumption is that the waste package will always be subject to sufficient stress to lead to cracking. Since some creep of the material might be expected over long disposal periods this is by no means certain to be the case. A second assumption is that the hydrogen will be evenly distributed as hydride precipitates throughout the material.

The criterion for failure by HIC then becomes the time required for the alloy to absorb this amount of hydrogen. In their ability to enforce repassivation within crevices the alloying elements must exist as, or create, catalytic cathodic sites. This raises the question as to whether, and in what form, these elements can catalyze the absorption of hydrogen into the Ti matrix. While this process could be rapid under propagating crevice conditions (Noël et al. 1996, Shoesmith et al. 1997), it will be much slower under passive conditions but could still be a factor if sufficiently cathodic polarization of titanium could be achieved.

The absorption of hydrogen into titanium is not readily achieved, since the oxide is highly impermeable, and it is necessary to induce, by cathodic polarization, redox transformations within the oxide. It is this need which accounts for the criterion of a potential < -0.7 V specified by Schutz and Thomas (1987), and demonstrated in long term hydrogen absorption measurements by Murai et al. (1977) (Figure 11). Figure 12 attempts to illustrate the nature of the parallel oxide redox transformation-hydrogen absorption process, which occurs once the potential is sufficiently negative of the flatband potential for surface degeneracy to be established. A more detailed discussion of this process has been given elsewhere (Shoesmith and Ikeda 1997).

Once the potential is sufficiently negative for these transformations to occur, titanium hydrides are thermodynamically stable with respect to the metal (Beck 1973) and the passive film can only be considered as a transport barrier. Beyond this threshold potential, the rate of absorption of hydrogen by the metal is effectively independent of potential down to ~ -1.0 V (vs SCE) (Figure 11). Indeed, there is a significant amount of evidence to claim that hydrogen is not transported through the oxide film at any significant rate until potentials < -1.0 V (vs SCE) are achieved. This is clearly evident in electrochemistry-in-situ neutron experiments on titanium (Figure 13). Hydrogen has a strong negative scattering length for neutrons and, when present in the oxide, reduces its scattering length density (Tun et al 1999). The results in Figure 13 show that hydrogen is present in the oxide close to the oxide/solution interface but not close to the metal/oxide interface, and that a cathodic polarization of > -1.0 V is required for hydrogen to penetrate to the metal/oxide interface when its entry into the metal becomes inevitable. A fuller discussion of these results is available elsewhere (Tun et al. 1999).

A more definitive demonstration that significant hydrogen transport through TiO_2 does not occur until E < -1.0 V (vs SCE) was obtained using an electrochemically controlled bilayer system comprising a layer of TiO_2 deposited on Pd metal (Pyun and Yoon 1996). By using this bilayer in back to back electrochemical cells, hydrogen could be injected into the TiO_2 at the TiO_2/solution interface ($H^+ + e \rightarrow H_{abs}$), and its transport detected by its reoxidation ($H_{abs} \rightarrow H^+ + e$) at the Pd/solution interface. Any H_{abs} crossing the boundary from TiO_2 to Pd is subsequently transported very rapidly to the Pd/solution interface and detected by oxidation. The results in

Figure 14 show that no detectable hydrogen transport through the TiO_2 layer into the Pd occurred until the potential applied to the TiO_2/solution interface was < -1.0 V (vs SCE). These results are consistent with industrial observations which show significant hydride formation and embrittlement of Ti is not observed until $E < -1.0$ V (Schutz and Thomas 1987).

The fear when alloying elements capable of catalyzing proton reduction are added to titanium is that they will also catalyze hydrogen absorption. If, for instance, intermetallic precipitates are present, over which a coherent layer of TiO_2 does not act as first a chemical, then a transport barrier, then possible "hydrogen windows" exist within the oxide. Under these circumstances, transformation of the redox properties of the passive oxide may not be a necessary prerequisite for hydrogen absorption, which could therefore occur at potentials more positive than -0.6 V. Whether or not this proves to be the case will depend on the catalytic properties of the cathodic sites, but, inevitably, the alloying elements added, Ni, Pd, Ru, are known to facilitate proton reduction (Greef et al. 1985) and to possess significant solubilities for hydrogen. An attempt to illustrate this scenario schematically is shown in Figure 15.

A substantial body of evidence exists to show that the presence of these alloying elements can lead to the absorption of hydrogen into titanium. This evidence is summarized, referenced, and discussed in Appendix A. The nature and distribution of the alloying element has a large effect on this behaviour. For Ti-12 (containing both Ni and Fe (as an impurity)) and Ti-2 (similarly contaminated with Fe) both the corrosion behaviour and the extent and rate of hydrogen absorption depend on the location and chemical form of the alloying element (Ni) and impurity element Fe.

Both Ni- and Fe-containing β-phase and Ti_2Ni and Ti_xFe intermetallic particles are susceptible to corrosion in acidic environments. The evidence in support of this claim is given in Appendix B. While it remains to be demonstrated whether Ni/Fe-containing β-phase can act as a catalytic cathode, there is little doubt in the case of the intermetallics, or in their ability to absorb hydrogen. Consequently, for sufficiently acidic conditions the corrosion of the β-phase or intermetallic will lead to hydrogen absorption. It is likely however, that absorbed H would remain localized at the intermetallic sites unless the predominately α-phase alloy contains β-phase ligaments, commonly located along α-phase grain boundaries, which enhance transport of hydrogen into the bulk of the alloy. An attempt to illustrate this process is given in Figure 16. In the absence of these transport pathways, the intermetallic particles may become saturated in H, a condition for which the efficiency of further hydrogen absorption appears to approach zero.

For the Pd-containing alloys, the formation of β-phase is negligible and intermetallic particles, when present, appear inert to corrosion (Appendix B). The rate and efficiency of hydrogen absorption increases with increasing Pd content, though, in the absence of any apparent separation of the Pd into discrete intermetallics (Ti-7), the mechanism of absorption remains unclear. Electrochemical evidence for catalysis of the proton discharge step,

$$H^+ + e \rightarrow H_{ads}$$

a characteristic feature of proton reduction on noble metals, is clear. Presumably, in the absence of separated intermetallic particles, this discharge step, and the subsequent H absorption step, occur at the atomic level. Since absorption can occur for $E > -0.6$ V, redox transformations within the oxide do not appear to be a prerequisite.

For Ti-16, H absorption was not observed for potentials as low as –1.0 V, despite the presence of a large number of randomly dispersed intermetallic particles (Appendix A). While the degree of catalysis of proton discharge and the efficiency of H absorption are expected to decrease as the Pd content decreases (i.e., from Ti-7 to Ti-16), this observation is still surprising. Since the material investigated contained a substantial amount of Fe (as an impurity) it is likely that the particles contain Fe. However, since they are apparently inert to corrosion in acidic solutions, which Ti_xFe is not, there is the possibility that Pd cosegregated to yield TiPdFe particles. The composition and properties of these particles remain to be elucidated.

4. CORROSION PROCESSES POSSIBLE UNDER WASTE REPOSITORY CONDITIONS

The discussion in this section is confined to an assessment of the possible corrosion behaviour of Ti alloys incorporated into the triple wall waste package design. An assessment of the anticipated corrosion behaviour of Ti alloys utilized as a drip shield is given in Appendix C.

From the discussion in the previous sections, it is clear that pitting will not be a failure mechanism and that active crevice corrosion, leading to waste package failure, is extremely unlikely for the alloys chosen. For Ti-12, the initiation of crevice corrosion would be possible, but any significant propagation would be prevented by repassivation of the alloy. This has been demonstrated even for high temperature conditions in very aggressive Mg^{2+}-containing brines. For the Ti-16 and Ti-7 alloys the possibility of active crevice corrosion is extremely remote. In the absence of active crevice corrosion, the most likely corrosion scenario for Ti under repository conditions is that it will absorb H in the occluded areas existing between inner and outer barrier walls of the waste package. For this to happen the Ti, or at least the intermetallics within it, must function as cathodes coupled to some anode within the system. For such a couple to be actively established the development of acidic conditions within these occluded areas would be required.

Three potential anodes appear possible:

(i) The presence in the alloy of a reactive phase or intermetallic; e.g., β-phase and/or Ti_2Ni in Ti-12;

(ii) Galvanic coupling to another waste package material. (Considering the proposed waste package design, this would be either nickel alloy-22 or 316 stainless steel);

(iii) General active or enhanced passive corrosion of Ti in the presence in the groundwater of F^-.

4.1 GENERATION OF ACIDITY WITHIN CREVICED SITES

A key question which must be answered when considering these three possibilities is whether acidic conditions can be generated within creviced (occluded) regions even though active crevice corrosion conditions cannot be established. Noël (1999) has already shown that, for tight crevices between Ti and Teflon spacers, crevice acidification did occur at 100°C. While these crevices were coupled to large Ti counter electrodes (to yield an anode/cathode ratio of ~ 1:40) which could have helped drive the acidification process, it is clear that the creviced Ti face became etched (Figure 17). This etching was observed on Ti-2 specimens exposed to neutral NaCl solutions prior to the initiation of active crevice corrosion, and on Ti-2 specimens exposed to neutral sulphate solutions on which crevice corrosion did not initiate. Etching was also observed on the creviced face of Ti-16 specimens in chloride solutions, again despite the maintenance of passivity.

The fall in resistance observed in impedance experiments on Ti-2 and Ti-12 when the temperature is increased to > 65°C (Appendix B and Figure B2) can be interpreted to indicate that a film breakdown/recrystallization process occurs once this temperature is exceeded. These results and this claim are consistent with those of Shibata and Zhu (1995). Breakdown/recrystallization leads to the introduction of grain boundaries, and possibly even more open pathways, by which metal dissolution can occur. Under occluded crevice conditions, this leads to cation hydrolysis and the development of local acidity as illustrated schematically in Figure 18. That this development of acidity precedes the initiation of crevice corrosion on Ti-2 has been clearly demonstrated by Noël (1999), and is the reason why the industrial guideline for avoiding crevice corrosion, i.e., the temperature must be < 70°C (Schutz and Thomas 1987), applies. For the Ti-16 and Ti-7 alloys the development of this occluded acidity does not lead to the initiation of crevice corrosion.

The need for film breakdown/recrystallization to produce localized acidity suggests that such an acidification process would require temperatures higher than ~65°C. However, even at temperatures in the range 25°C to 35°C, a drop in pH of a few units from neutral (7) has been observed in laboratory-formed femoral taper crevices between Ti6Al4V and Cr-Co-Mo alloys (Gilbert and Jacobs 1997).

4.2 PASSIVE OXIDE DISSOLUTION

Under neutral conditions passive oxide dissolution rates are immeasurable (Mattsson and Olefjord 1990, Mattsson et al. 1990). Over a 6-year exposure period to water-saturated bentonite clay at 95°C, the maximum dissolution rate was < 0.4 nm/year. This value effectively represents an analytical detection limit since no dissolved Ti was found.

For more acidic conditions, Blackwood et al. (1988) measured dissolution rates of passive titanium oxides using electrochemical methods that determined the amount of oxide removed from the metal surface rather than by attempting to measure the amount of dissolved Ti^{3+}/Ti^{4+} in solution. These rates were measured in acidic sulphate, perchlorate, phosphate and chloride solutions at 45°C and, generally for pH = 2, (Table 3). Dissolution was chemical in nature; i.e., did not involve electrochemical interaction between the oxide and the substrate metal, and led to the uniform thinning (as opposed to pitting) of the oxide film. The rate was close to first order with respect to proton concentration. Extrapolation of these rates according to this pH dependence predicts negligibly small dissolution rates in neutral solutions, consistent with the observations of Mattsson and coworkers.

TABLE 3

RATES OF OXIDE DISSOLUTION AT 45°C
(from Blackwood et al. 1988)

Electrolyte	Concentration ($mol \cdot dm^{-3}$)	Dissolution Rate (μm/year)
H_2SO_4	3.0	19.53
H_2SO_4	1.0	16.12
H_2SO_4	0.25	8.15
H_2SO_4	0.02	2.01
$H_2SO_4/NaHSO_4$	1.0/1.0	11.21
H_2SO_4/K_2SO_4		2.72
H_3PO_4	3.0	2.60
$HClO_4$	3.0	9.2
HCl	3.0	17.17
Oxalic acid	1.0	12.52

Within an acidified crevice (at 45°C), these rates indicate that a maximum rate of 10-20 μm/year for a pH ~ 1 falling to < 1-2 mm/y for pH ~ 2 would be possible. Clearly, substantial and enduring acidification would be required for passive dissolution rates at creviced sites to reach significant values.

4.3 EFFECT OF FLUORIDES

The corrosion of Ti and its alloys in the presence of F^- has mainly been studied for dental and flue gas scrubber applications. In the first application the environment is saline and neutral, but low temperature, and in the second much more aggressively saline, hot (> 100°C) and potentially acidic. For the low temperature dental applications, Ti-2 was tested in 1% NaCl solutions ranging in pH from 6 to ~3 containing between 1000 and 100 μg/g of F^- (Reclaru and Meyer 1988). For flue gas scrubber applications the environments tested were much more concentrated with Ca and $MgCl_2$ concentrations between 0.1 and 12.7% (i.e., [Cl^-] up to 15,700 $\mu g \cdot g^{-1}$ with [SO_4^{2-}] in the range 9000 to 26,000 $\mu g \cdot g^{-1}$). The temperature was up to 177°C and the pH down to ~1. Fluoride concentrations were in the range 0 to 12,000 $\mu g \cdot g^{-1}$ (Thomas and Bomberger 1983, Schutz and Grauman 1986). These concentrations are similar to those used in corrosion testing (Table 4) and those established in J-13 well water evaporation tests (Table 5).

TABLE 4

SIMULATED CORROSION TEST ENVIRONMENTS FOR THE YUCCA MOUNTAIN REPOSITORY

Parameter	Concentration (μg·g-1)						
	SDW (60°C)	SDW (90°C)	SCW (60°C)	SCW (90°C)	SAW (60°C)	SAW (90°C)	SCMW (60°C)
pH	9.5	9.9	9.2	9.2	2.7	2.7	7.8
Ca^{2+}	3.5	3.4	16	15	58	58	400
Mg^{2+}	1.2	ND	29	3.4	52	53	4
K^+	36	38	4600	4,500	4,300	4,3000	85
Na^+	430	460	36,000	44,000	43,000	43,000	10
Si	17	16	18	58	30	50	10
SO_4^{2-}	170	180	13,000	13,000	41,000	40,000	1,200
Cl^-	68	74	7,4000	7,500	28,000	27,000	11
NO_3^-	62	64	7,000	7,200	23,000	24,000	10
F^-	14	15	300	1,400	0	0	<0.1
HCO_3^-	720	700	44,000	51,000	0	0	<1
Equiv. NaCl	112	122	12,199	12,363	46,157	44,508	18

ND – not detected
SDW – simulated dilute well water (10×J-13)
SCW – Simulated concentrated well water (1000×J-13)
SAW – simulated acidified well water
SCMW – simulated cement-modified water

In the dentistry related studies in 1% NaCl containing ~ 1000 $\mu g \cdot g^{-1}$ of F^- passivity was maintained, and the galvanic currents generated by coupling to various Au/Ag dental alloys were insignificant (1 to 10 $nA \cdot cm^{-2}$) (Reclaru and Meyer 1988). Although it is not made specifically clear it appears that Ti formed the cathode in these couples. When galvanically coupled to 316L stainless steel a galvanic current of ~ 400 $nA \cdot cm^{-2}$ was obtained with Ti acting as the anode. As will be seen when discussing the galvanic coupling of Ti below, this observation (i.e., Ti acting as the anode) is not uncommon. In the absence and presence of F^- the potential of this couple was 9 mV and –30 mV (vs SCE), respectively. In neither case is the potential sufficiently negative to allow H absorption by Ti-2. When the pH is decreased, the presence of F^- leads to an increase in passive current density, and, under creviced conditions the potential drops to much more negative values, indicating that in the presence of F^-, crevice corrosion of Ti-2 could occur even at low temperatures.

TABLE 5

EXPECTED GROUNDWATER CONCENTRATIONS AFTER WETTING/EVAPORATION CYCLES

		Concentration (mg/L)		
Ion	J-13	Long Term Test Solution 1000x	Beaker Evaporation 1000x	90°C/85%RH
SO_4	18.4	13000	15700	29500
Cl	7.14	7200	6120	14800
NO_3	8.78	6440	6730	14200
F	2.18	1580	1520	3400
HCO_3	128.9	47326	31471	
Na	45.8	42500	37700	77400
K	5.04	3580	3720	9700
Ca	13.0	3	7	25
Mg	2.01	1	0	0
$SiO_{2(aq)}$	61.0	109.14	7124	22500
pH	7.4	10.1	9.9	10

Long term test solution - similar to SCW in Table 4
Beaker evaporation - J-13 solution evaporated to 1000x concentration in the presence of crushed tuff
90°C/85%RH – Evaporation performed for a constant relative humidity

In the simulated flue gas scrubber environments, the influence of F^- was much more muted (Thomas and Bomberger 1983, Schutz and Grauman 1986). As observed in the dental studies, the passivity of Ti-2 was lost for pH < 3 when F^- was present. For Ti-12 this pH-threshold for the loss of passivity was < 1.5. Although Ti-16 and Ti-7 were not tested, it would be expected from these observations that an even lower pH would be required before F^- exerted any significant influence on these two alloys. An interesting synergism was observed between Cl^-

and F^-, the influence of F^- on corrosion decreasing as $[Cl^-]$ increased (Thomas and Bomberger 1983). This was attributed to a common ion effect with Ca^{2+} leading to the precipitation of CaF_2. The presence of flyash eliminated any influence of the F^- ion, an effect attributed to the introduction of Fe^{3+}, a known inhibitor of Ti corrosion, and to the presence of SiO_2 which would complex F^-, thereby reducing its free concentration drastically.

At concentrations of ~ 100 $\mu g \cdot g^{-1}$, Schutz and Grauman (1986) found that F^- did not influence the electrochemically-determined repassivation potentials for Ti-2, Ti-12 and Ti-7 at 82°C for pH values as low as 1.5. Values remained > 7 V (vs SCE). Crevice corrosion tests showed no susceptibility except at 177°C, and for Ti-7 passivity was maintained even at this temperature. In tests involving a galvanic couple to carbon steel, only Ti-12 showed any significant H absorption. Some enhancement of H absorption was noticed for Ti-7 galvanically-coupled to carbon steel, but only when the couple was driven under oxidizing conditions and presumably when the additional demand for cathodic current was partially met by proton reduction.

More general laboratory studies have concentrated on strongly acidic solutions, when the influence of fluoride (as HF) is significant in the millimolar range (10-100 $\mu g \cdot g^{-1}$). Wilhelmsen and Grande (1987) concluded that acidic fluoride (HF) stimulated the passive dissolution of titanium at these concentrations, but that the F^- ion had no effect on passive behaviour. Their electrochemical data clearly indicates that F^- will only be aggressive in acidic solutions. This conclusion was supported by Auger spectroscopy measurements which showed that incorporation of F^- into the passive film leading to increased passive currents and increased film thicknesses only occurred at low pH (~ 0). Unfortunately, no experiments were conducted at slightly higher pHs than 0. In alkaline solutions (pH ~ 13), no influence on passive currents or incorporation into the oxide was observed.

This pH dependence of the influence of F^- is consistent with expectations for the dissolution of oxides. If F^- is to accelerate the transfer of Ti^{4+} to solution (as TiF_6^{2-}) then it must be accompanied by the neutralization of O^{2-} ions by H^+. As the pH increases one would expect the latter anion transfer process to become rate determining, and hence for the ability of F^- to accelerate TiO_2 dissolution to decrease (Segall et al. 1988).

The possibility of an aggressive F^- solution developing within a crevice on the waste package seems unlikely. While crevice acidification is to be expected, and recent beaker and evaporation tests (Table 5) show F^- concentrations could reach 3400 $\mu g \cdot g^{-1}$, a number of factors suggest this will not lead to particularly aggressive consequences. Firstly, for significant temperatures (60 to 90°C) HF could be sufficiently volatile to prevent its concentration in solutions. Secondly, the concentration of other groundwater species will impede the development of extreme acidic conditions within the crevice, and nullify the ability of F^- and Cl^- to produce active crevice conditions.

Both sulphate and carbonate suppress crevice corrosion by neutralizing acidity (Shoesmith et al. 1995b). The buffering ability of HCO_3^- is obvious, while that for SO_4^{2-} is more likely due to its ability to complex dissolved Ti^{III}/Ti^{IV} species, thereby preventing their hydrolysis to produce protons. Also, SO_4^{2-} enhances the ability of Ti to maintain passivity by an autopassivation process. This autopassivation process couples the reduction of Ti^{IV} to Ti^{III} with active metal dissolution, and its acceleration in SO_4^{2-}-containing solutions reinforces passivity (Kelly 1982). This ability of SO_4^{2-} to drive the repassivation of Ti was observed by Sedriks (1975) on Ti-Ru (0.1 to 0.3%), but misinterpreted as the ability of dissolved Ru to redeposit to form catalytic cathodes. In boiling H_2SO_4, he observed a decrease with time of the corrosion rate to effectively zero. A similar decrease in boiling HCl was not observed. This drop in rate is clearly an anion effect, and not a consequence of the accumulation in solution of dissolved Ru. It can be attributed to the build up of sulphate-complexed Ti^{IV} which eventually enforces repassivation. Since Cl^- does not complex Ti^{4+} as strongly as SO_4^{2-}, the Ti^{4+} reduction step is much slower and repassivation much more difficult to enforce (Kelly 1982).

Our own experiments on Ti-2 crevice corrosion (Shoesmith et al. 1995b) clearly indicate the ability of SO_4^{2-} to suppress active crevice corrosion and cause repassivation when present in excess over Cl^-. Given the significant sulphate concentrations likely to exist within waste package crevices (Tables 4 and 5) the dominance of SO_4^{2-} over Cl^- and F^- can be expected.

A final feature which could nullify any adverse influence of F^- within waste package crevices would be the presence of substantial amounts of silica. Evaporation testing under a condition of constant relative humidity (90°C/75% RH, Table 5) lead to the formation of a silica gel. While unproven, it was claimed that, in the flue gas scrubber tests (Thomas and Bomberger 1983, Schutz and Grauman 1986), SiO_2, present as flyash lead to a reduction in the free concentration of F^- and the elimination of its influence on titanium corrosion.

4.4 GALVANIC COUPLING TO OTHER MATERIALS

Many instances of galvanic corrosion have been documented when titanium is coupled to other materials. The coupling of Ti to active metals, such as Zn, Mg, Al and carbon steel are well documented and have the potential to cause hydrogen absorption and the possibility of eventual embrittlement when the temperature is in excess of 80°C (Schutz and Thomas 1987). The coupling of Ti to less active materials such as Al bronzes (Cheng et al. 1993) and Cu-Ni alloys (Shifler et al. 1997) can also lead to the enhanced corrosion of the coupled material. These last couples have been shown to function under saline conditions, in particular, in seawater. Although no conclusive evidence is available, it seems unlikely that these couples can achieve galvanic corrosion potentials sufficiently cathodic to induce significant hydrogen absorption by the Ti. However, in the absence of a good understanding of how the alloying additions influence the hydrogen absorption properties of the alloys Ti-12, Ti-7 and Ti-16, the possibility of hydrogen absorption, while unlikely, cannot be definitively ruled out.

The possibility of galvanic corrosion decreases markedly when the coupled material is passive (Shifler et al. 1997, Peacock 1998), since the corrosion potentials for such materials (measured in seawater) are generally very close. This is the case for the materials of interest in waste package applications (Table 6). The closeness of the galvanic potentials makes it difficult to decide which material in the couple will act as the cathode and which the anode, but negligible galvanic interaction should occur as long as passivity is maintained.

According to Schutz (1986), Ti should generally be the cathode in galvanic couples, but Reclaru and Meyer (1988) have shown Ti to be the anode when in contact with a series of dental alloys, although the galvanic currents were extremely low. Wang et al. (1999) also reported that Ti-2 could form the anode or cathode when coupled to various materials in hot (50°C to 90°C) 6% NaCl. Brass and alloy 600 were found to anodically polarize Ti, while 316 stainless steel and Monel could polarize Ti either anodically or cathodically depending on temperature and pH. However, the reliability of these last results is uncertain since it is not clear whether the pretreatment of the specimens used in the experiments caused their surface hydriding or not, or whether similarly polarized couples would be obtained for alternative geometries and coupled surface areas.

TABLE 6

GALVANIC SERIES IN FLOWING SEAWATER
(4 m/s) at 24°C; from Schutz 1986)

Material	Corrosion Potential (V vs SCE)
Ti	-0.10
316 SS (passive)	-0.05
304 SS (passive)	-0.08
Alloy C (passive)	-0.08
316 SS (active)	-0.18
314 SS (active)	-0.53

When ions, such as sulphides, which can interfere with passivity are present, then galvanic coupling of Ti to generally passive materials such as stainless steels can occur (Peacock 1998). Thus, Foroulis (1989) found that Ti could form either the anode or the cathode in galvanic couples depending on the aggressiveness of the solution to which the couple was exposed, although the test environments used were not really relevant to waste repository conditions. The tests were generally conducted in hot (80°C) acidic sulphate and sulphidic solutions (pH = 0.5 to 5) or in ammonium sulphide solutions (pH 9-10.6). Whether or not the Ti was the anode or cathode depended on whether chlorides or cyanides were present. When these ions were present Ti tended to be more cathodic by 200 to 300 mV. This was attributed to the loss of passivity on the coupled material due, in this case to the breaking of a sulphide film, when Cl^- was present. In sulphidic solutions containing CN^- and Cl^-, the Ti tended to be cathodic and the corrosion rates of carbon steel, 304 stainless steel and I-600 were enhanced by a factor of 1 to 2. In solutions free of CN^-, Ti was anodic to these materials and no adverse corrosion effects were observed on either of the materials in the couple.

What is clear from this discussion is that galvanic couples involving Ti and other passive materials are unlikely to lead to significant corrosion of either material. The prospect of a galvanic couple between titanium and alloy-22 leading to any significant damage of either material can be judged remote. However, given the corrosion potential for 304 stainless steel when active in seawater (Table 6) the possibility of Ti being the cathode in a couple with this material is a possibility in an acidified crevice containing a concentrated groundwater, e.g., SAW in Table 3. Whether or not stainless steel can become active under these conditions remains to be determined. For significantly negative potentials (-0.53 V vs SCE, Table 6) to be established would require the active crevice corrosion of the stainless steel not just the establishment of low density pitting, a condition for which such negative potentials should not be established. However, it would be judicious, given this possibility, to choose a stainless steel resistant to crevice corrosion, if the possibility of a crevice with Ti is unavoidable.

5. SUMMARY AND CONCLUSIONS

The possible failure processes, crevice corrosion, pitting and hydrogen-induced cracking (HIC) have been reviewed for the candidate titanium alloys (Ti-12, Ti-16 and Ti-7) under anticipated conditions in the Yucca Mountain nuclear waste repository. Both pitting and crevice corrosion are extremely remote possibilities under these conditions for these alloys. For Ti-12 it is possible that a limited amount of crevice corrosion could occur but repassivation has inevitably been observed after ~ 1 mm of penetration in even the most aggressive of saturated brines.
All three alloys could suffer hydrogen absorption making the possibility of hydrogen-induced cracking worth investigation. Based on slow strain rate testing of pre-hydrided compact tension specimens, both Ti-12 and Ti-16 have been shown capable of tolerating a substantial hydrogen concentration before any decrease in fracture toughness is observed. For Ti-12 the fracture toughness starts to decrease once the hydrogen content reaches a value of ~ 400 $\mu g \cdot g^{-1}$, whereas for Ti-16 this threshold is at least ~ 1000 $\mu g \cdot g^{-1}$. It may be larger for Ti-16 but testing has so far been limited.

The feature which determines whether this degradation in fracture toughness will lead to waste package failure is the rate of hydrogen absorption by the alloy. For the commercially pure Ti-2 hydrogen absorption is extremely slow, and probably negligible, for potentials more positive than –0.6 V (vs SCE). This potential coincides with that required to induce the redox transformation, Ti^{4+} to Ti^{3+}, in the passive TiO_2 oxide, a process that renders the oxide conductive and permeable to hydrogen. Generally, such a potential is only achieved when titanium is over-protected cathodically, or galvanically coupled to an actively corroding metal such as carbon steel.

However, the presence of intermetallics in the alloys under consideration (and possibly also β-phase in Ti-12) could allow hydrogen absorption into the metal at potentials less negative than this –0.6 V threshold. Both Ti-12 and Ti-7 have been shown to absorb hydrogen at potentials above this threshold, but the few experiments performed to date on Ti-16 indicate that no absorption occurs until < -1.0V. This last alloy definitely contains many randomly dispersed intermetallic particles. To date their identity has not been elucidated, and why they do not appear to act as hydrogen absorption sites not determined.

From this review it was concluded that the only feasible failure mechanism for these titanium alloys, when used in the triple wall waste package design, would be hydrogen absorption leading to HIC within an acidified crevice under passive conditions. For this to occur the titanium would need to act as a cathodic site and would require a coupledanode.

The titanium could supply its own anode in two ways.

The intermetallic could be corrosive under acidified crevice conditions thereby acting as both anode and cathode. The intermetallic Ti_2Ni (in Ti-12) has been demonstrated capable of acting in this manner, and Ti-12 has been shown to more readily absorb hydrogen than the commercial alloy, Ti-2. However, the intermetallic particles in Ti-16 appear to be inert, a claim based on impedance measurements. Consequently, they would not be expected to be corrosive in the same manner as Ti_2Ni in Ti-12, and hence incapable of providing an anodic site.

The presence of F^- in the concentrated groundwaters anticipated at Yucca Mountain could accelerate passive dissolution, and hydrogen could be absorbed at the cathodic intermetallic site. For this to be feasible, the pH would have to be < 3 (for Ti-2) with substantial amounts of F^- present. The evidence from dental and flue gas scrubber experiments indicates that this can occur but is unlikely in the presence of the other groundwater anions expected to be present, particularly SO_4^{2-} and HCO_3^-, and in the presence of substantial amounts of silica. These last three species inhibit the development of acidity within crevices and, in the case of silica, appear to remove F^- from the solution. There is also the possibility that, under acidic elevated temperature conditions, F^- may be removed as the volatile HF. For the alloy Ti-12, a pH < 1.5 appears necessary before F^- exerts any measurable influence on the passive corrosion rate. Although not tested one would, therefore, expect an even lower pH threshold for the Ti-16 and Ti-7 alloys. At the levels anticipated on the waste packages in Yucca Mountain, F^- should not exert a significant influence on the corrosion of Ti-12, Ti-7 and Ti-16, but definitive proof is presently unavailable.

The third potential anode could be provided by the coupling of a more active material to the passive titanium. Within the present waste package design this would be either Alloy-22 or 316L stainless steel. If all the three materials remain passive, then it is possible the Ti alloys could be either anodes or cathodes in the couple. Evidence exists to show both combinations are possible and that the activities of the couples are generally innocuously low. However, the test environments have not been as aggressive as those anticipated at Yucca Mountain. While it is unlikely that Alloy-22 will form an active anode, the possibility cannot presently be ruled out with stainless steels. In environments where the passivity of the stainless steel can be degraded (sulphidic environments have been tested), galvanic couples to Ti were observed and the steel corrosion rates accelerated, but only by a factor of 1 to 2.

The formation of such a galvanic couple would be expected to lead to the absorption of hydrogen by the Ti-12 and Ti-7 alloys but possibly not by the Ti-16 alloy. For Ti-12, absorption would be expected to be more extensive than with the other alloys, and the transport of absorbed hydrogen into the bulk of the alloy facilitated by the presence of β-phase ligaments along predominantly α-phase grain boundaries. Since the efficiency of hydrogen absorption decreases as the Pd content of the alloy decreases, Ti-16 would be expected to absorb hydrogen less readily than the Ti-7 alloy. Indeed, some speculative evidence exists suggesting that the intermetallic particles presence in Ti-16 may prevent absorption.

Based on these studies the order of preference of these alloys as candidate materials for waste packages at Yucca Mountain would be

Ti-16 ≥ Ti-7 >> Ti-12

However, before a confident recommendation that Ti-16 be chosen over Ti-7, a real understanding of the presently baffling behaviour of the intermetallic particles in this material is required.

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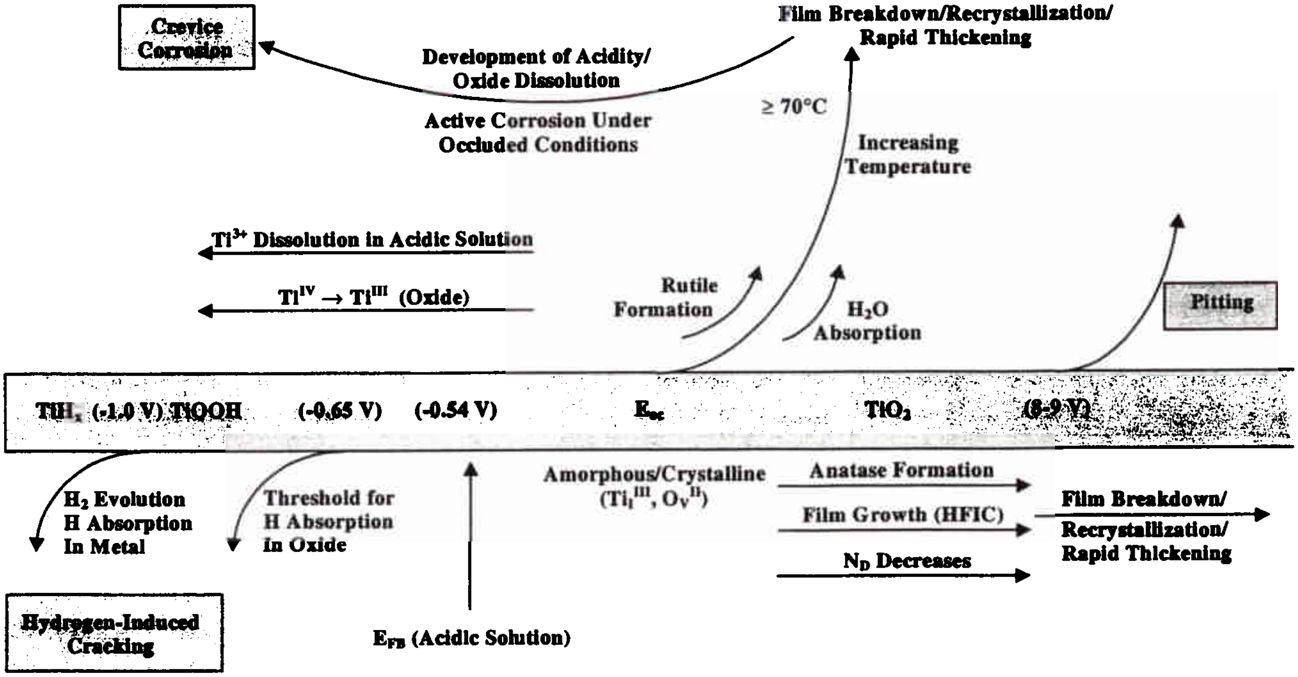

Figure 1: Summary of the Changes Expected in Passive Oxide Properties as a Function of pH, Potential and Temperature

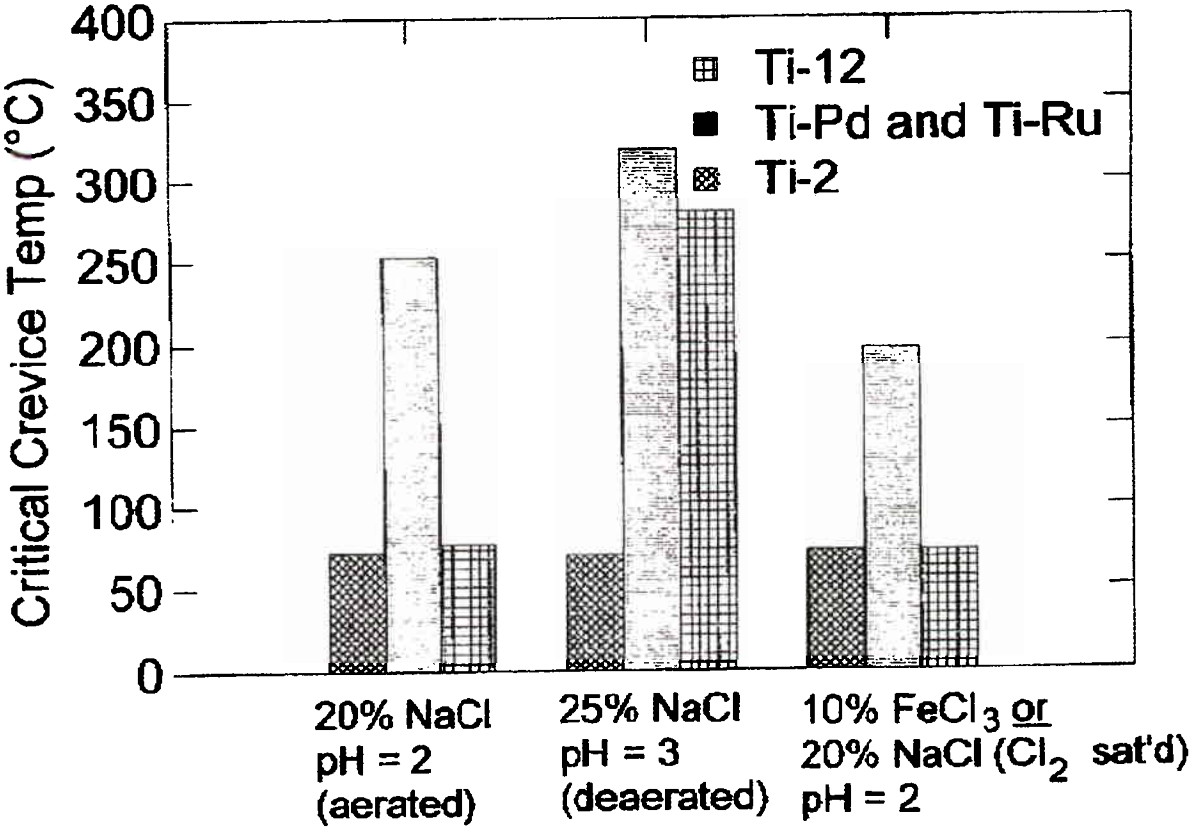

Figure 2: Critical Crevice Temperatures for Ti-12, Ti-16 and Ti-7, and the Closely Related Ti-Ru Alloy, Determined in a Number of Aggressive Acidic and Extremely Oxidizing Chloride Environments (Reported From Schutz 1995)

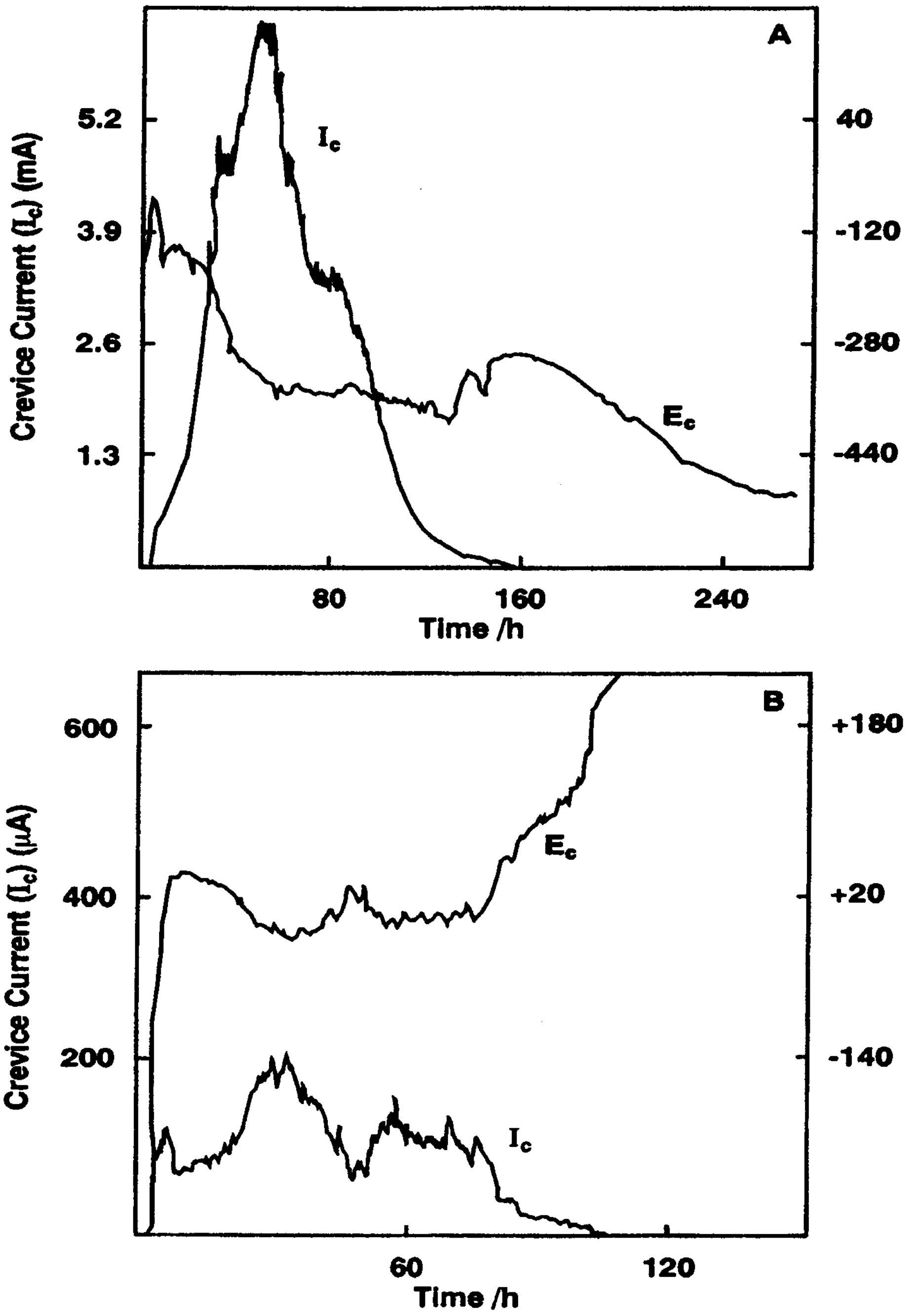

Figure 3: Coupled Currents (I_c) and Crevice Potentials (E_c) Measured in 0.27 mol·L^{-1} NaCl on Artificially Formed Crevices of Various Ti-Alloys: (A) Ti-2 (Fe-0.024 wt.%) at 150°C; (B) Ti-2 (Fe-0.13 wt.%) at 150°C;

continued...

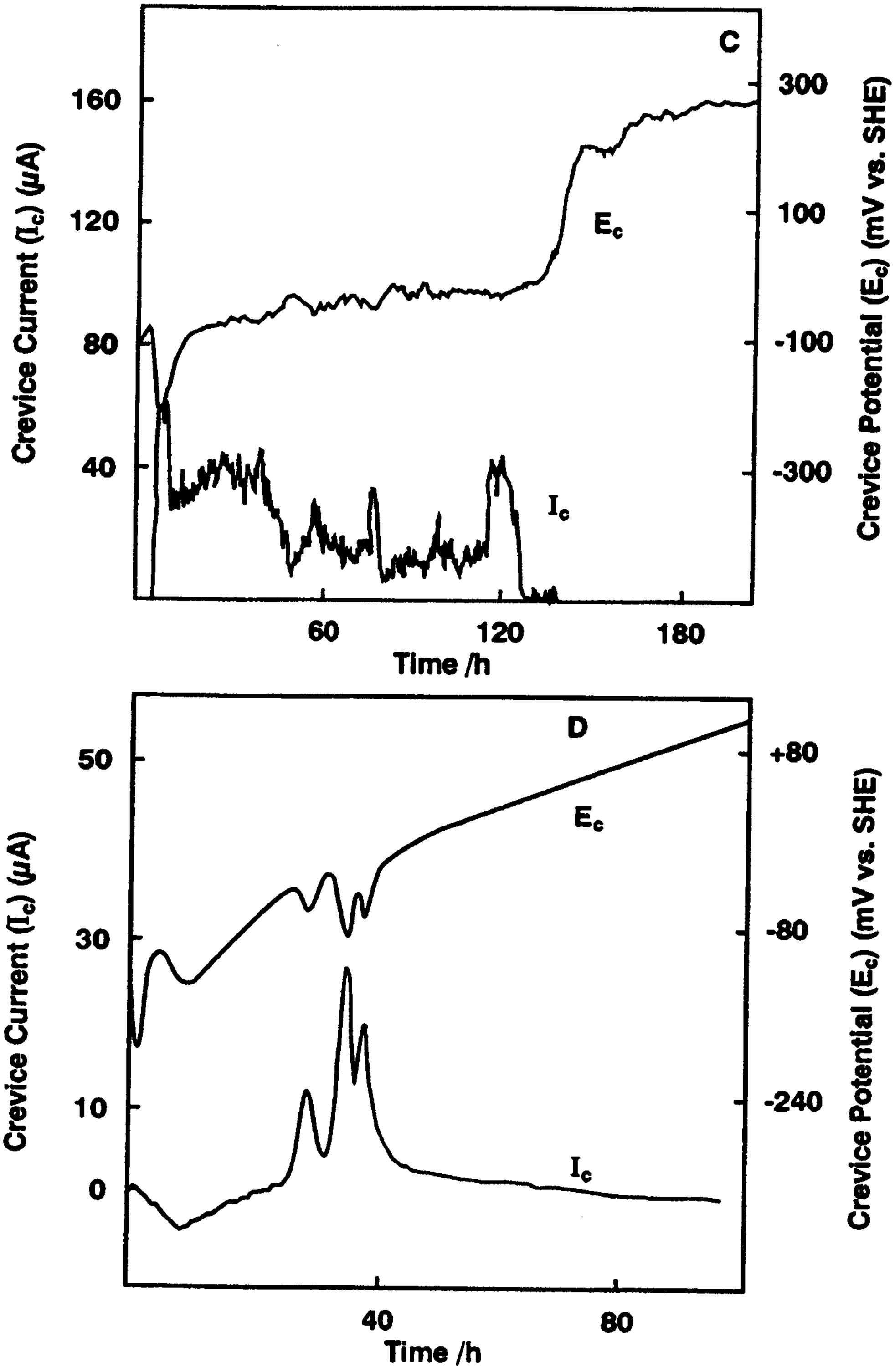

Figure 3: Coupled Currents (I_c) and Crevice Potentials (E_c) Measured in 0.27 mol·L^{-1} NaCl on Artificially Formed Crevices of Various Ti-Alloys: (C) Ti-12 at 150°C; (D) Ti-16 at 100°C (from Shoesmith et al. 1997)

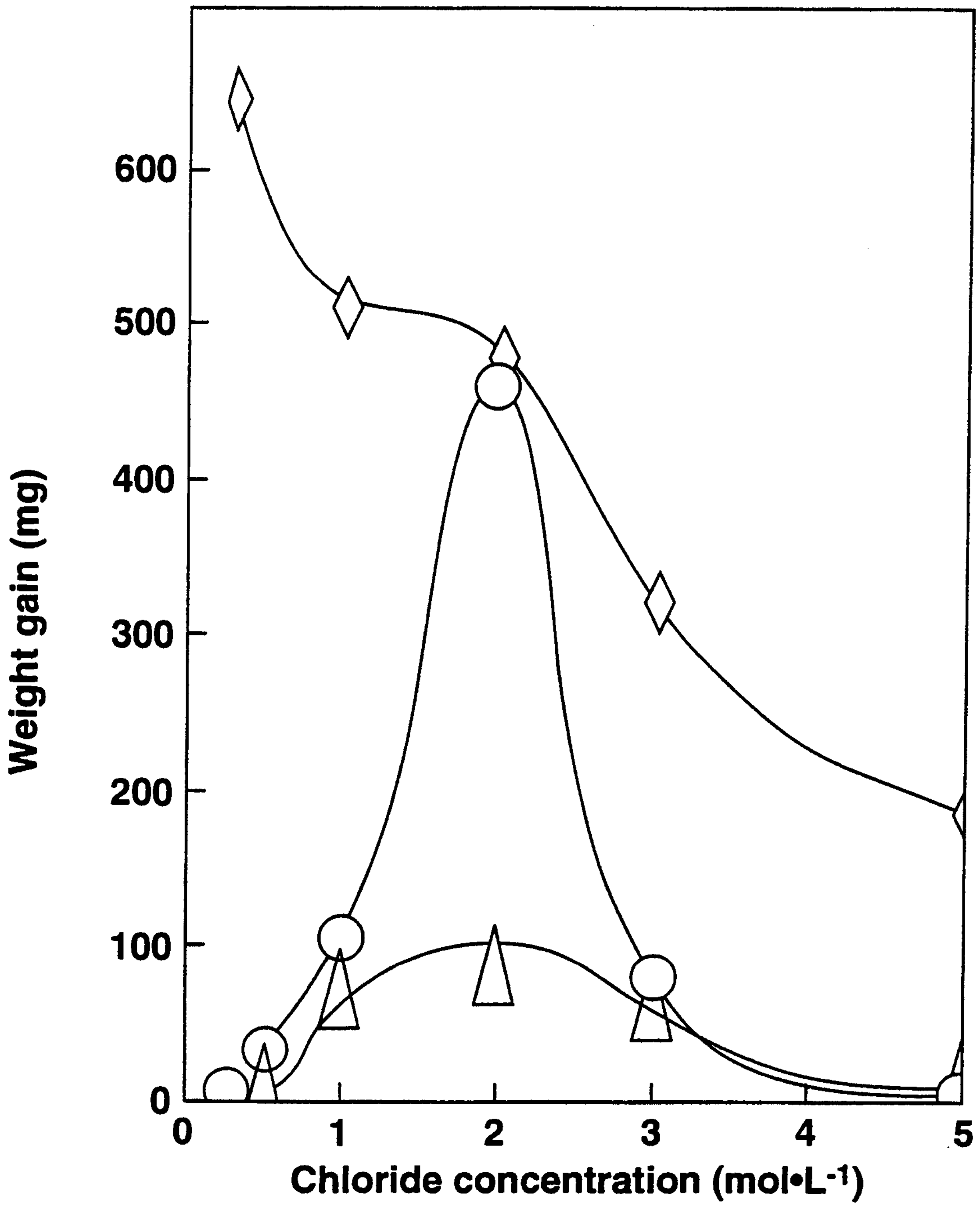

Figure 4: Weight Changes Due to Crevice Corrosion for Ti-2 (Diamonds, Low Iron Content), Ti-2 (Circles, High Iron Content) and Ti-12 (Δ) as a Function of Chloride Concentration at 150°C (from Bailey et al. 1996)

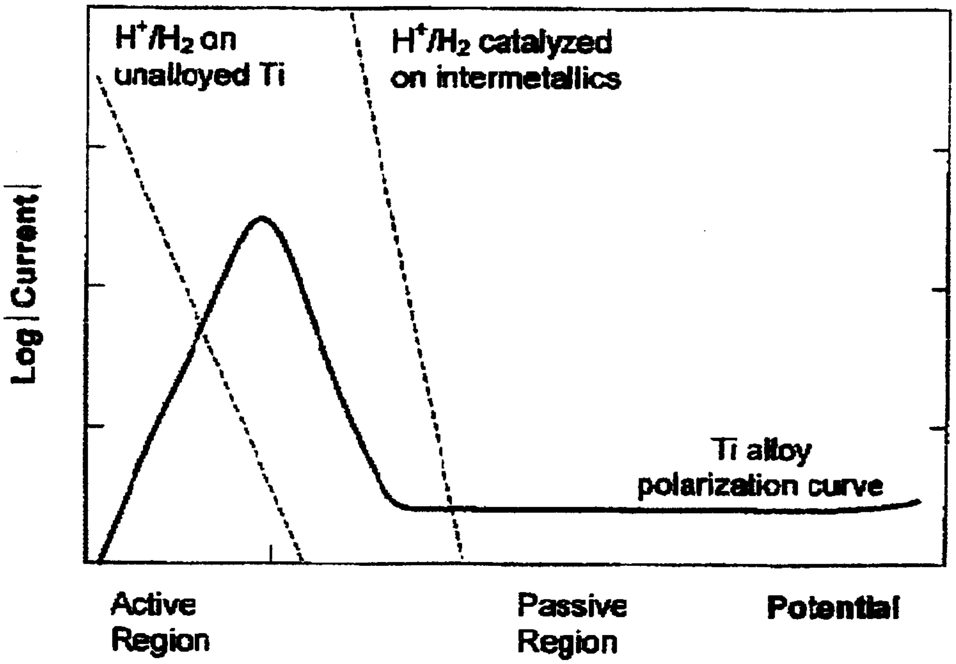

Figure 5: Schematic Illustrating the Polarization Curve for Titanium and its Relationship to the Cathodic Polarization Curves for Proton Reduction on Ti-2 and on a Titanium Alloy Containing a Catalytic Alloying Element (e.g., Ti-12, Ti-16)

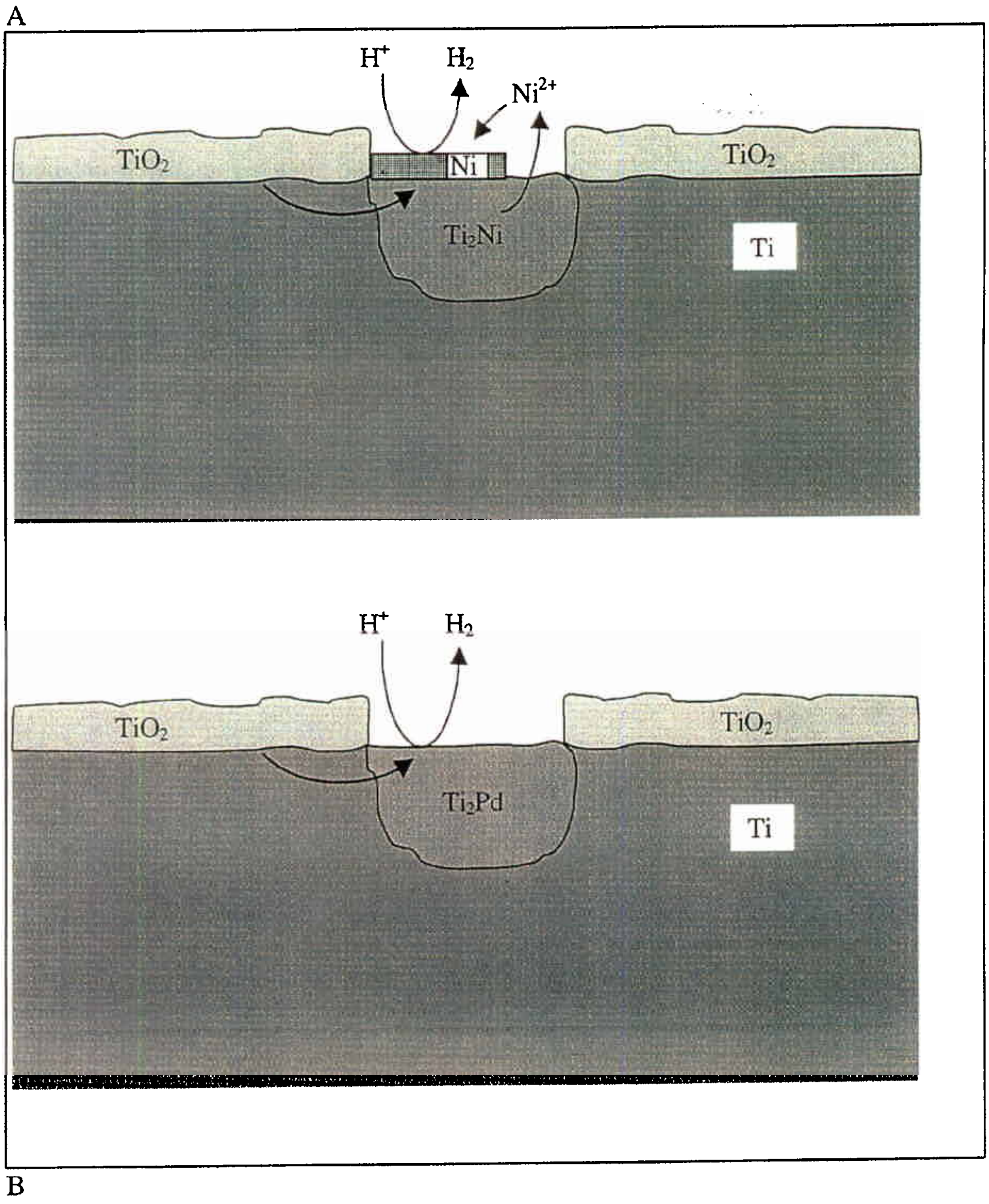

Figure 6: Schematics Illustrating the Two Mechanisms Proposed to Explain the Crevice Corrosion Resistance Conferred on Ti by Alloying With Ni (Ti-12) or Pd (Ti-7, Ti-16): Redeposition of Dissolved Alloying Element to Produce a Galvanically-Coupled Catalytic Site for H^+ Reduction; Galvanic Coupling of an Inert Catalytic Site for H^+ Reduction

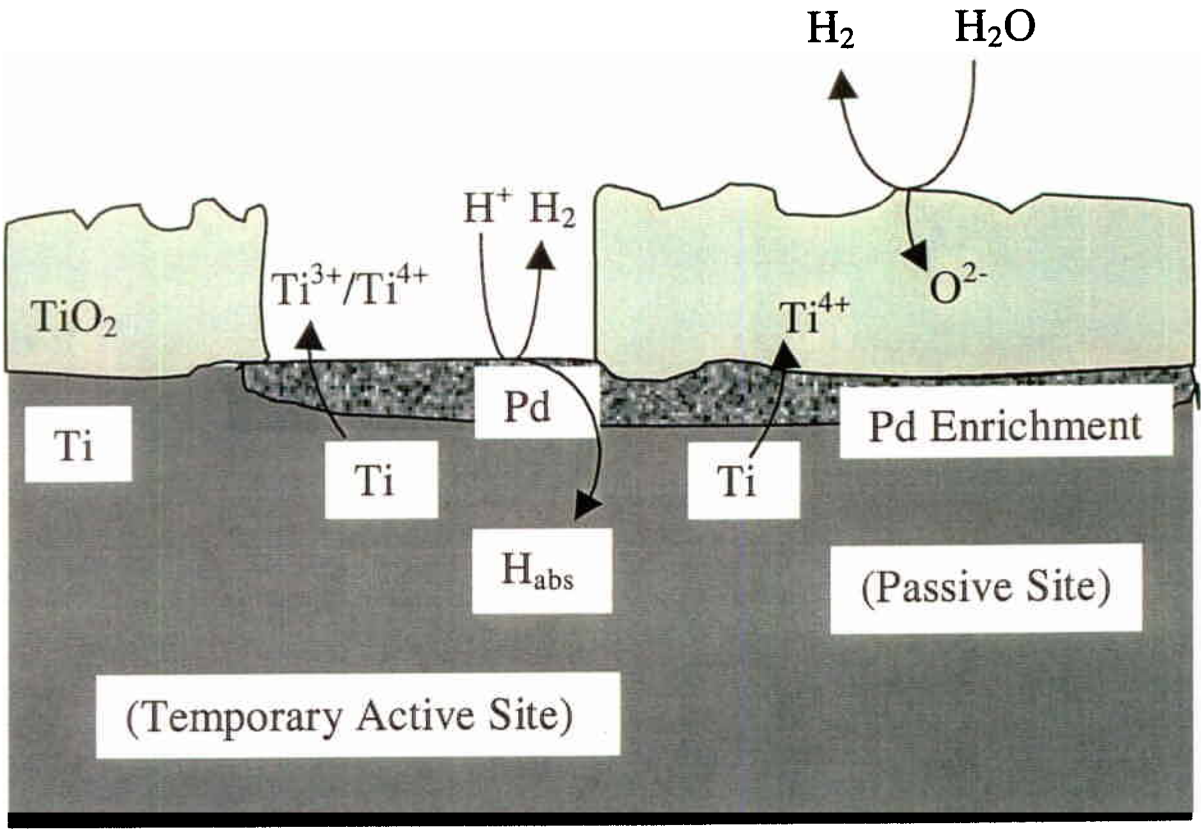

Figure 7: Schematic Illustrating the Anodic Ennoblement of a Pd-Containing Ti-Alloy Due to Surface Enrichment by Pd of Temporarily Active or Passive Sites

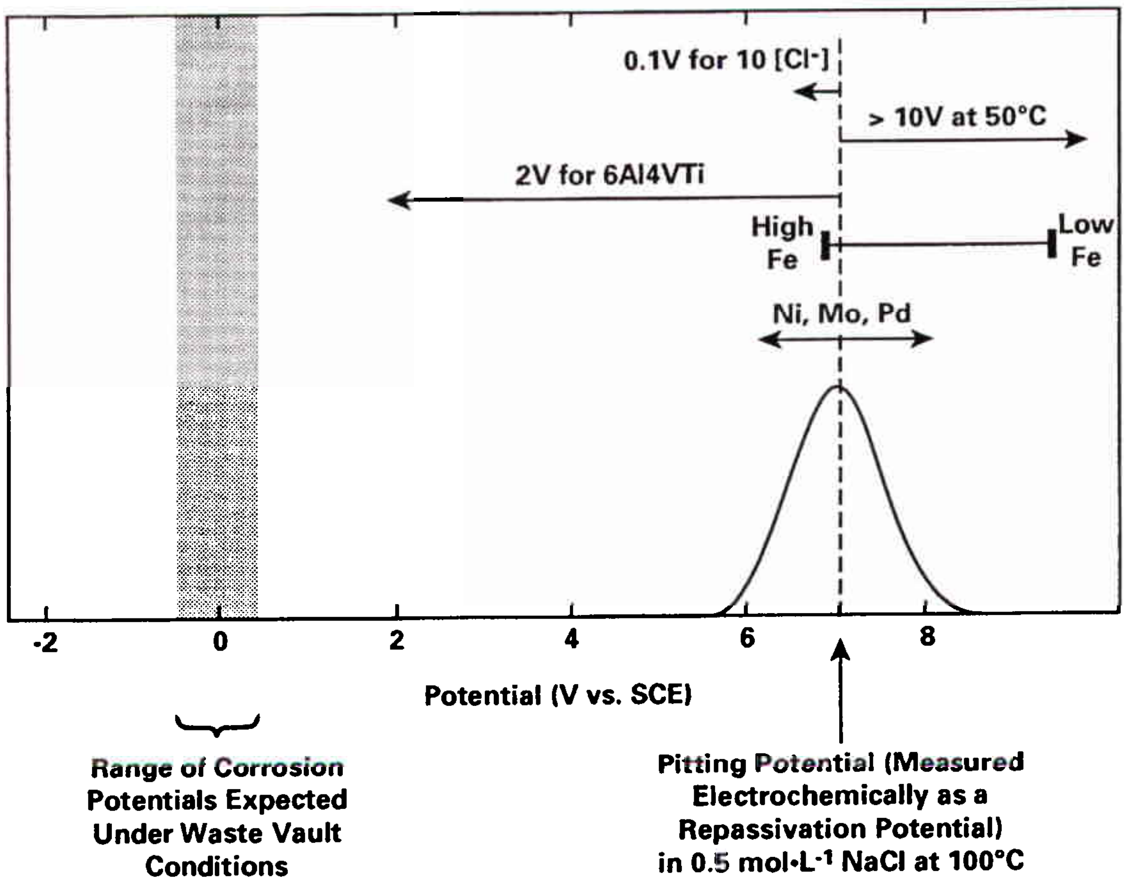

Figure 8: Summary of the Effect of Various Parameters on the Pitting Potential for Ti (from Shoesmith et al. 1997)

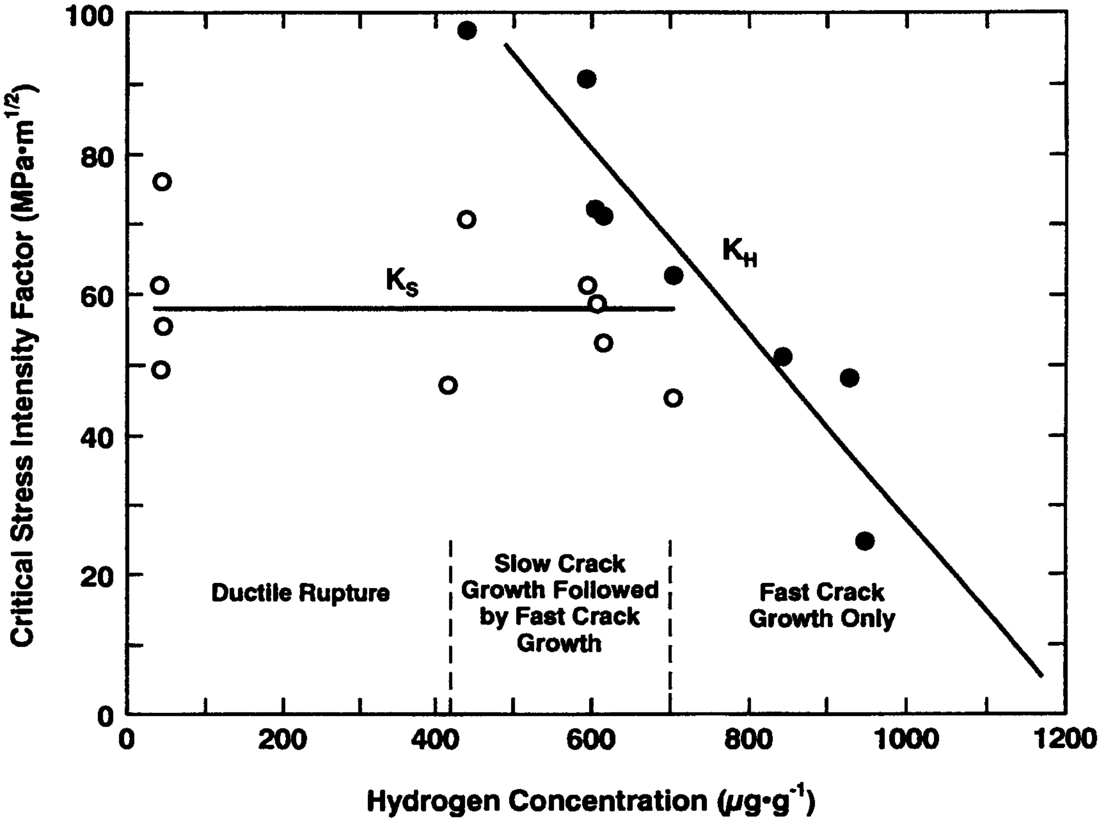

Figure 9: Variation of the Critical Stress Intensity Factor With Hydrogen Content for Ti-2 (Transverse-Longitudinal (T-L) Orientation): o – Slow Crack Growth (K_s); • - Fast Fracture (K_H) (from Clarke et al. 1994)

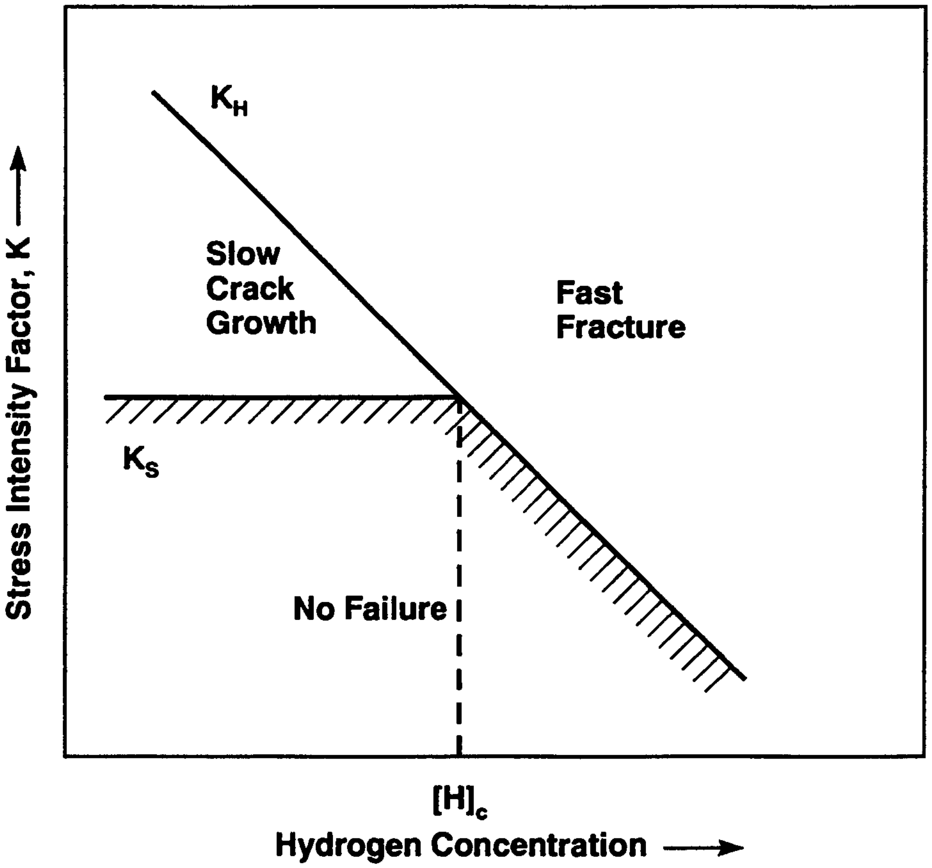

Figure 10: Schematic Showing the Combinations of Stress Intensity Factor and Hydrogen Concentration Leading Either to Fast Crack Growth (Brittle Failures (K_H)), Slow Crack Growth (K_s) Due to Either Sustained Load Cracking or Ductile Rupture, or to no Failure (from Shoesmith et al. 1995)

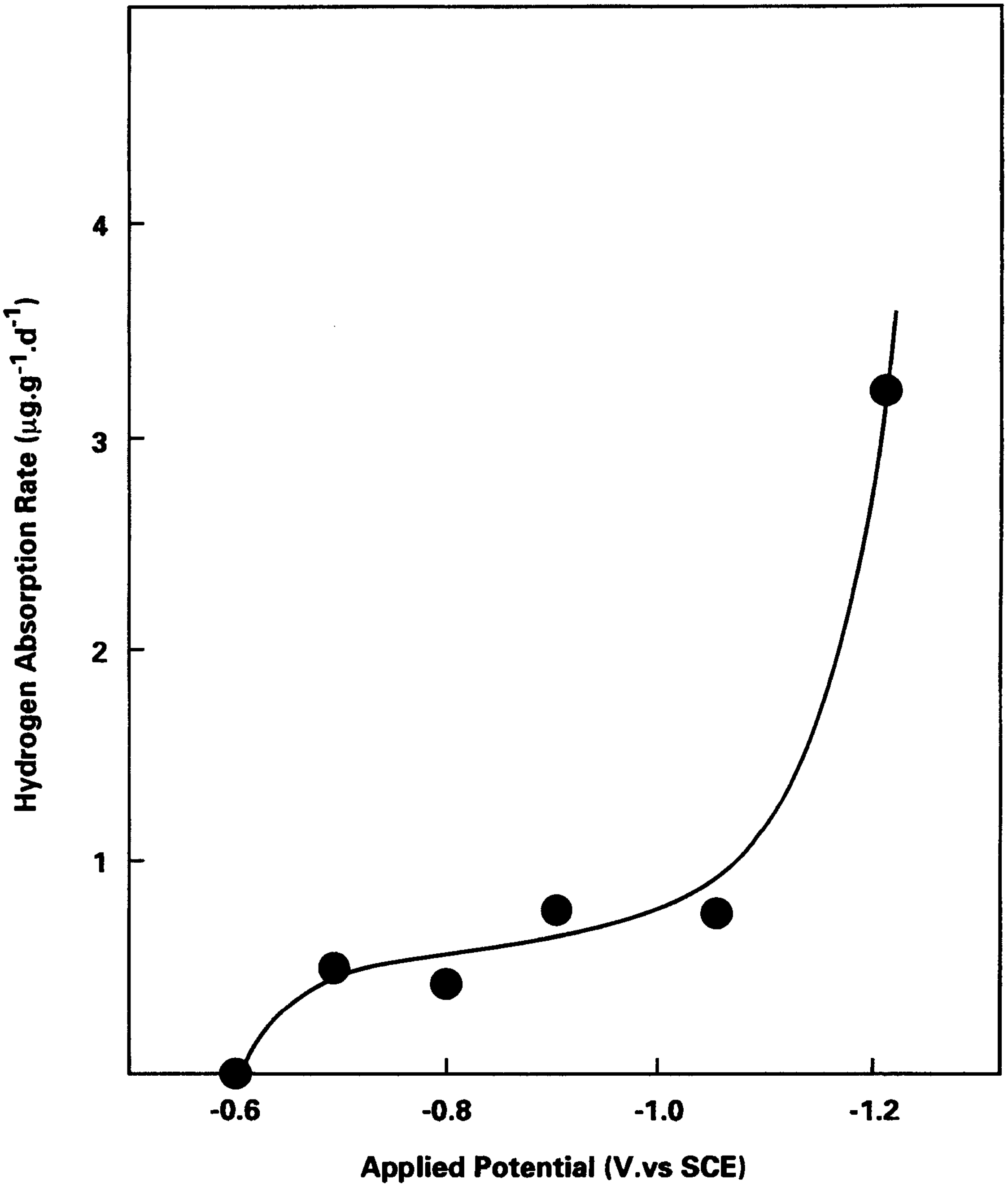

Figure 11: The Hydrogen Absorption Rate as a Function of Applied Potential Measured on Ti-2 Electrodes in Flowing Artificial Seawater With a Flow Velocity of 2.0 ms^{-1} at 30°C (from Murai et al. 1977)

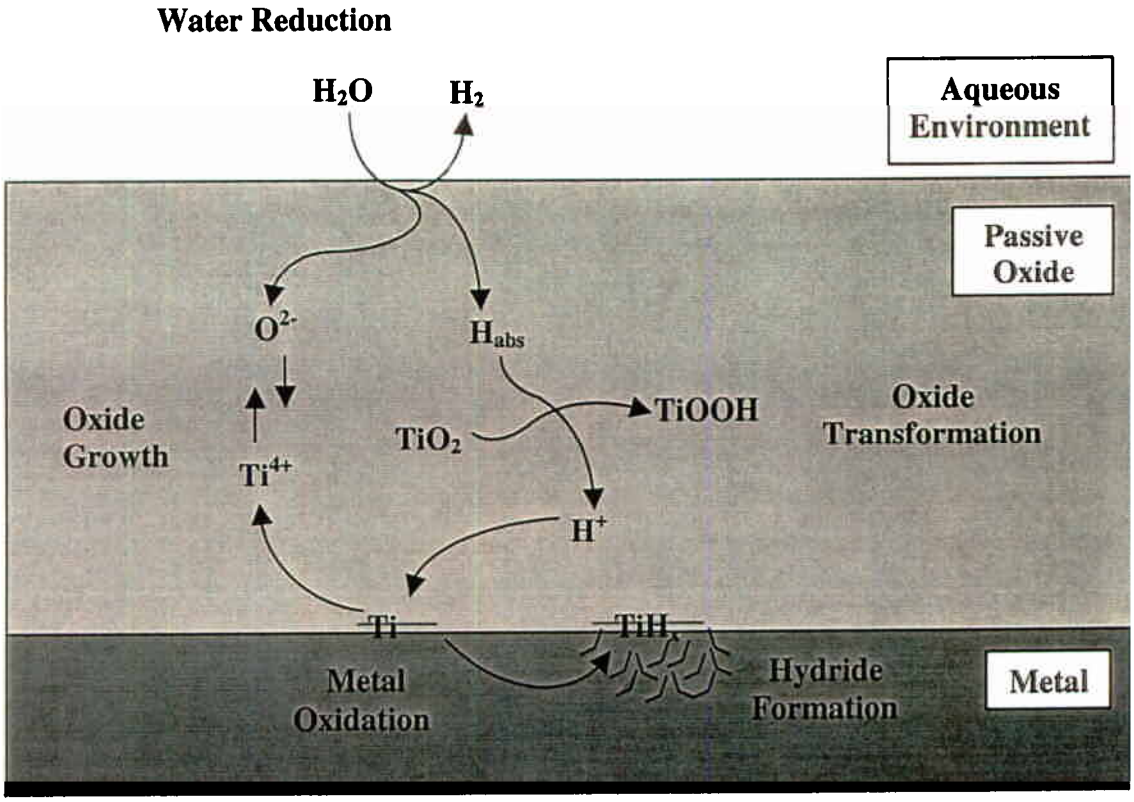

Figure 12: Schematic Illustrating the Cathodic Transformations Occurring in TiO_2 Films Which Lead to the Absorption of Hydrogen

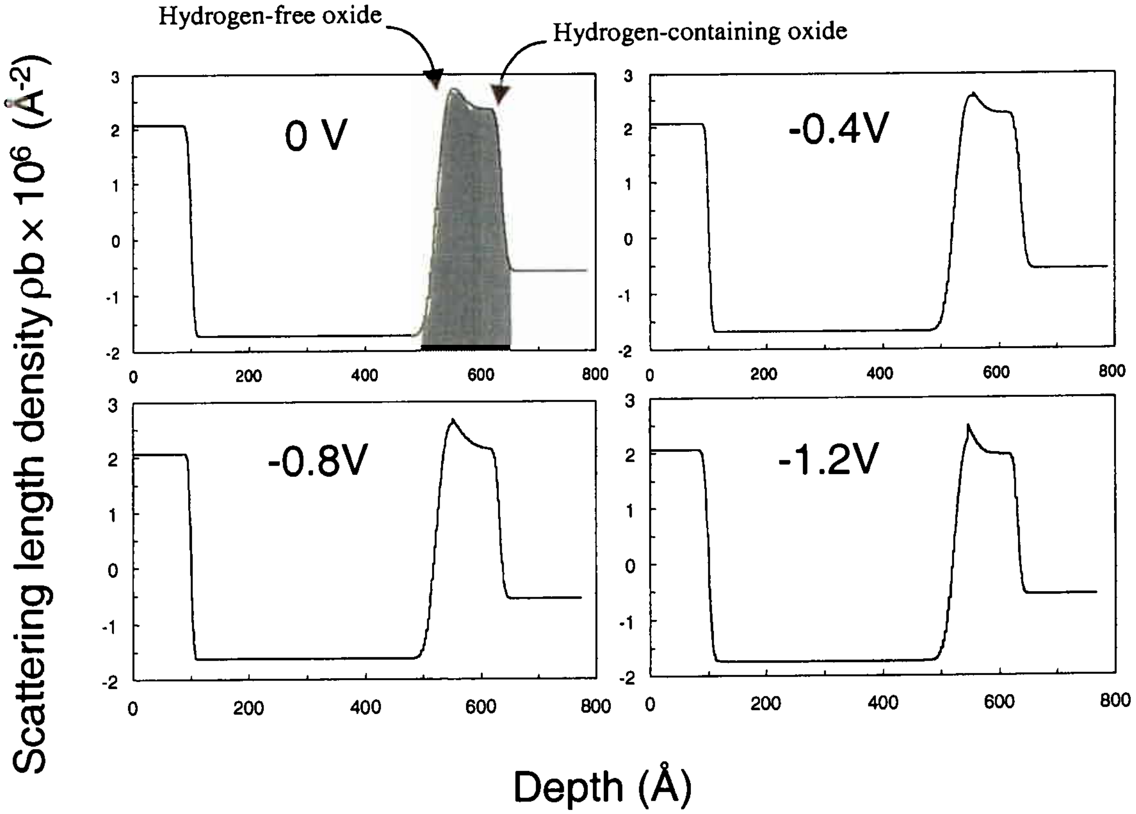

Figure 13

Figure 13: Profiles of Scattering Length Density (SLD) as a Function of Depth Recorded by In-Situ Neutron Reflectometry on an Anodically Treated (2.0V) Sputter-Deposited Ti Film in Neutral 0.2 mol·L^{-1}NaCl. While the SLD was being measured the electrode was potentiostatted at the indicated potentials. The differently shaded areas show the oxide region free of hydrogen and that containing hydrogen (from Tun et al. 1999).

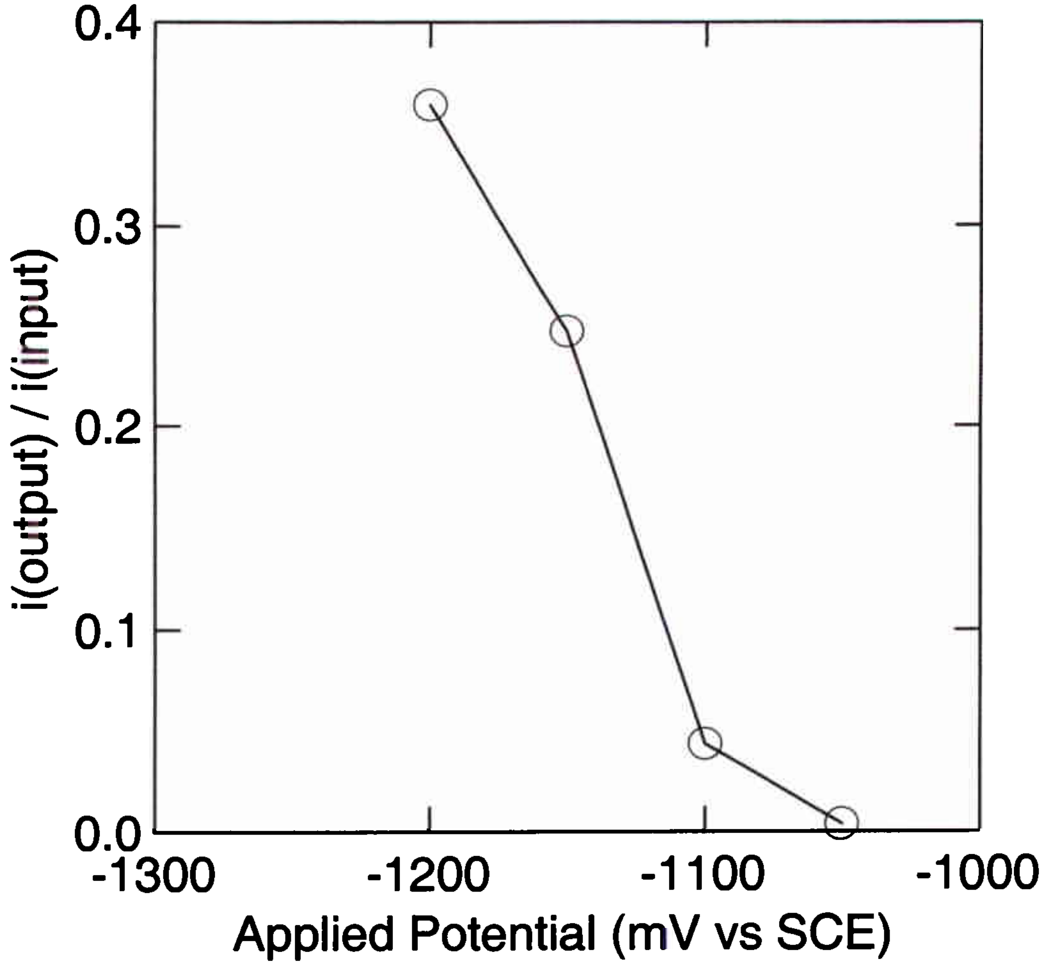

Figure 14: The Ratio of the Input Current to Output Current as a Function of the Potential Applied Across a TiO_2 Layer Deposited on Pd Metal. The ratio was measured in 0.1 mol·L^{-1} NaOH. The input current is the current measured for H^+ reduction at the TiO_2/solution interface. The output current is that measured for H oxidation across the Pd/solution interface (from Pyun and Yoon 1996).

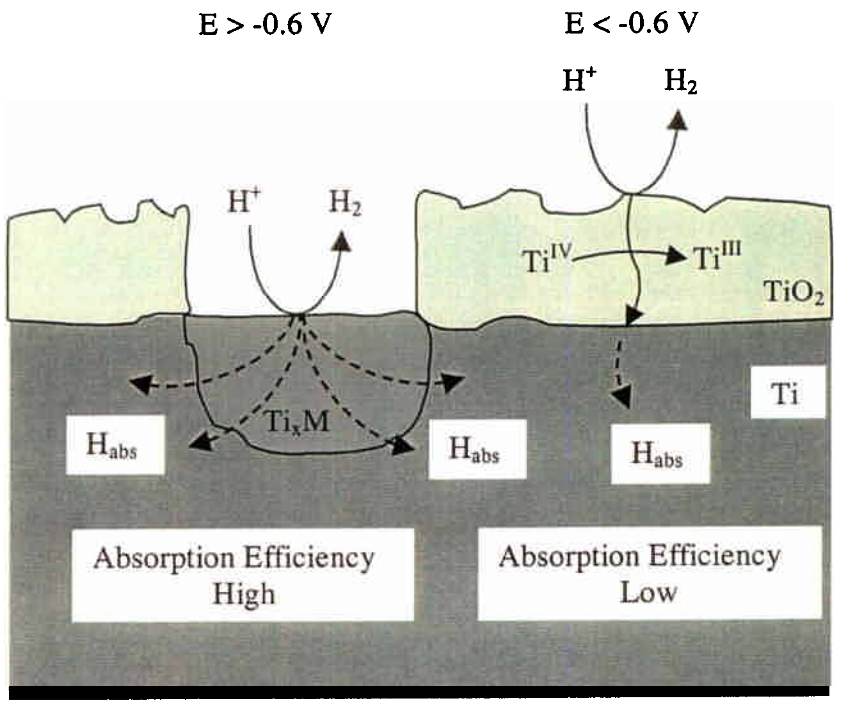

Figure 15: Schematic Illustrating the Low Efficiency of Hydrogen Absorption Under Passive Conditions and the Possibility of a Much More Highly Efficient Absorption Process Through Catalytic Intermetallic Windows in the Passive Oxide

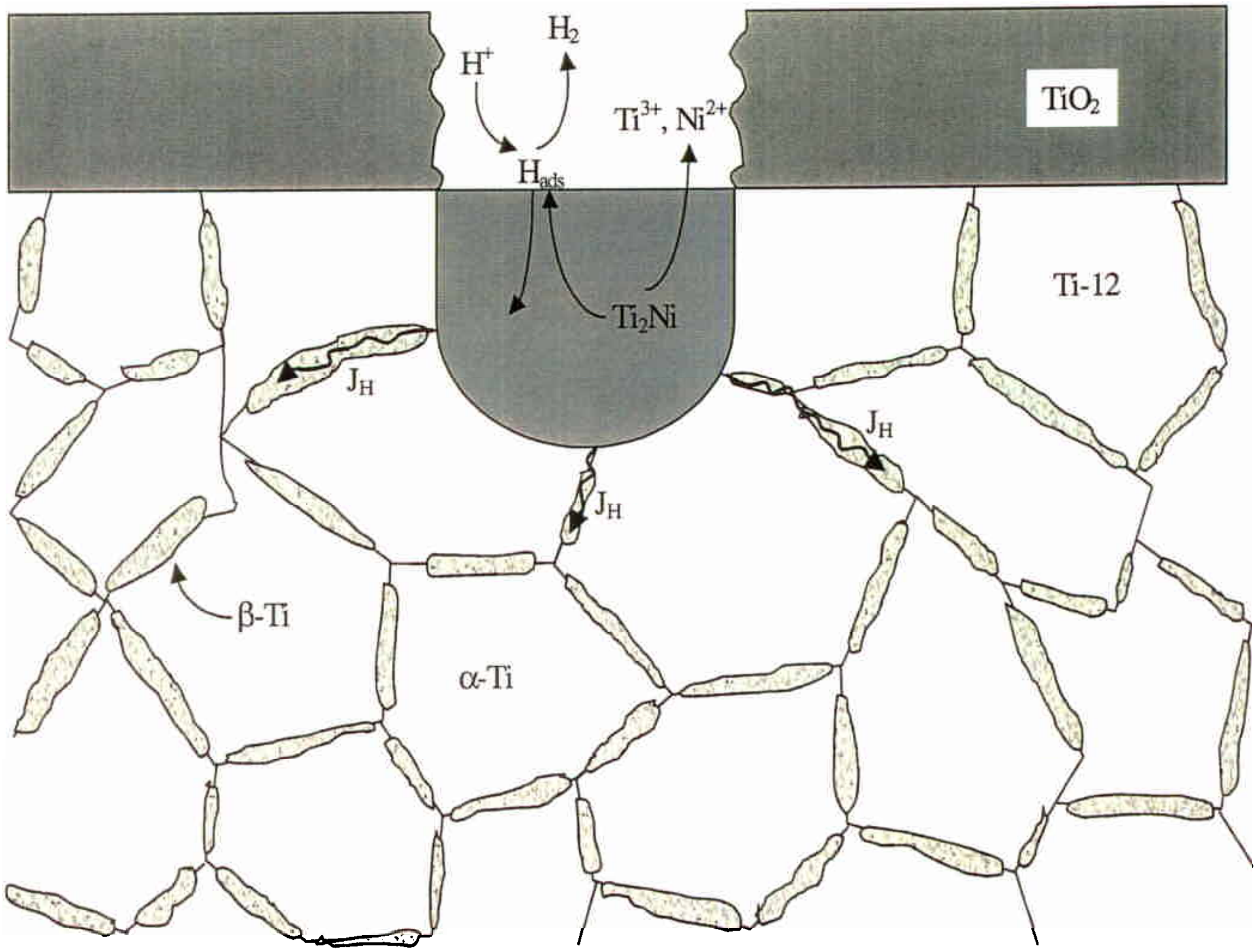

Figure 16: Schematic Illustrating How the Corrosion of a Ti_2Ni Intermetallic Particle Can Lead to the Absorption of Hydrogen and How the Presence of β-Phase Ligaments Along α-Phase Grain Boundaries Can Assist the Transport of This Absorbed Hydrogen Into the Bulk of the Alloy

Figure 17: The Creviced Face of a Ti Specimen Exposed to 0.27 mol·L^{-1} NaCl at 100°C Without the Initiation of Active Crevice Corrosion. The rectangular area between the two bolt holes shows the section of the titanium beneath the PTFE crevice former. The darkened area within this creviced area is the stained area due to the development of acidic conditions within the crevice.

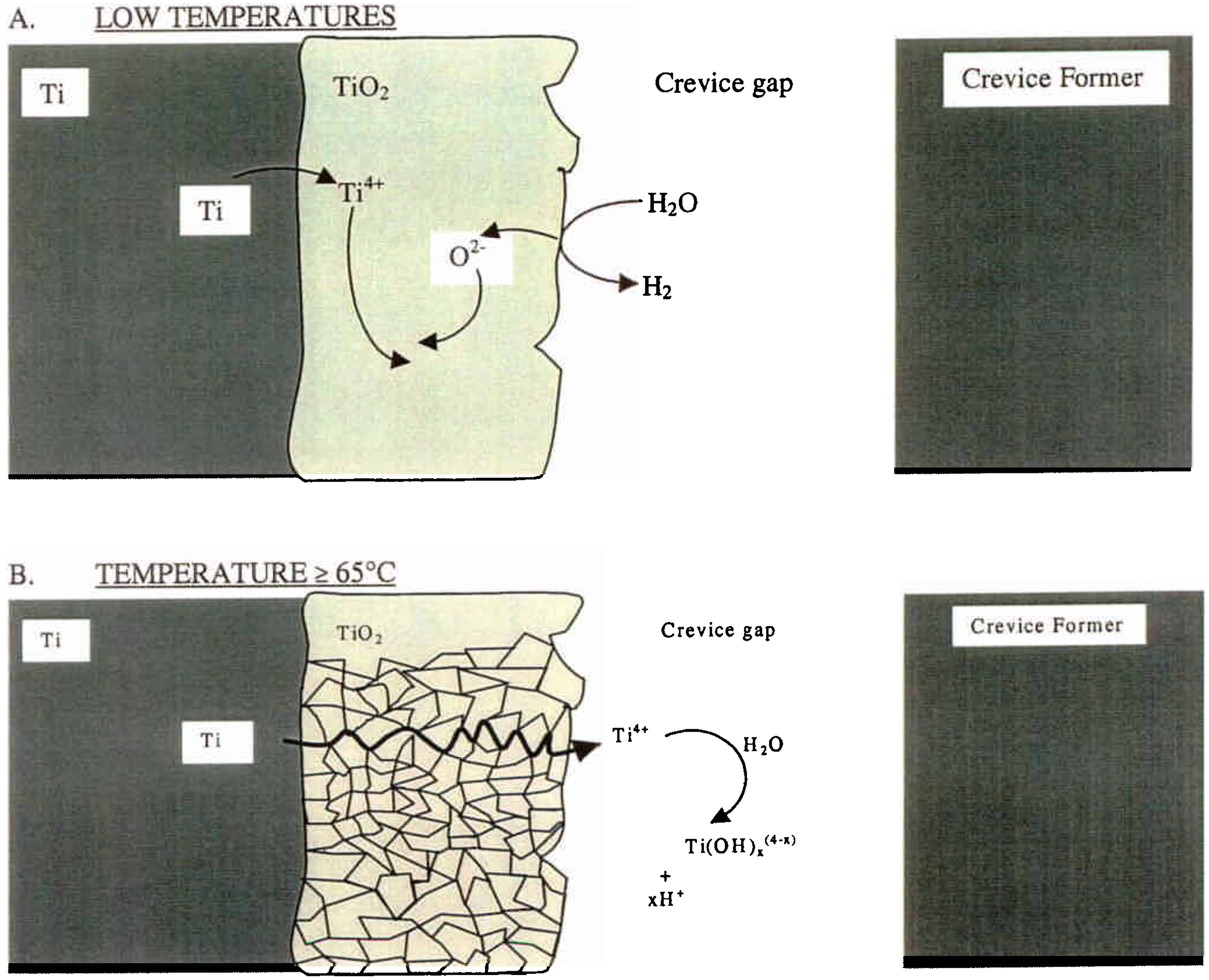

Figure 18: Schematics Illustrating the Processes Occurring Within a Creviced Site at, (A) Low Temperature (< 65°C), and (B) Temperatures Greater Than 65°C. At low temperatures, film growth predominates and passivity is maintained. At higher temperatures, film breakdown/recrystallization processes occur leading to cation hydrolysis and the development of acidity within the creviced site.

APPENDIX A:

THE PROPERTIES OF ALLOYING ELEMENTS IN α-TITANIUM ALLOYS AND THEIR ABILITY TO CATALYZE HYDROGEN ABSORPTION

While the addition of alloying elements such as Ni (in Ti-12) and Pd (in Ti-16 and Ti-7) are generally beneficial in maintaining the passivity of the alloys, their cathodic properties make them potential catalysts for hydrogen absorption into the alloy.

A substantial body of evidence exists to show that the presence of these alloying elements leads to the absorption of hydrogen. Based on polarization curves determined in acidic solutions, Figure A1, Glass (1983) clearly showed that Ti_2Ni and titanium could couple galvanically. In a subsequent experiment, in which commercially pure Ti was coupled to Ti_2Ni in boiling HCl, he showed that the dissolution of Ti was accompanied by the embrittlement of the Ti_2Ni, and concluded that the cathodic kinetics on Ti-12 (containing Ti_2Ni) would be dominated by proton reduction on Ti_2Ni providing a sufficient surface area of the intermetallic were available. Okada (1983) showed that Ni-plated (by electrodeposition) or Pt-coated (by sputter deposition) titanium electrodes readily absorbed hydrogen for $pH < 3$, efficiencies of up to 60% being obtained in acidic solutions at 25°C, Figure A2. At 40°C, the efficiency[1] for absorption rose to over 80%. Clearly, the formation of Ni or Pd (which will be as catalytic as Pt) deposits during crevice corrosion, Figure 6A, would be expected to enhance hydrogen absorption. Whether such high efficiencies could be achieved by galvanic coupling under neutral conditions will depend on the local chemistry conditions achieved at the cathodic site; i.e. at the intermetallic or exposed b-phase.

Kim and Oriani (1987) observed hydrogen absorption by Ti-12 at 25°C in a saturated brine with a high Mg^{2+} content. Even though gamma radiation was present in some of these experiments, hydrogen absorption occurred more rapidly when it was absent. In these brines the corrosion of Ti proceeds almost linearly when determined as the rate of oxide thickening. This is almost certainly a consequence of the corrosivity of such brines in which the high Mg^{2+} content allows only the formation of a defective oxide film (Shoesmith and King 1999). It is worth noting that, despite the fact corrosion continued unabated, the rate of hydrogen absorption decreased with time. This observation would suggest that perhaps, with long exposure times, H absorption would stop. Possible reasons for this could be saturation of the available surface absorption sites; i.e. the intermetallics and/or b-phase and, hence, both a decrease in absorption efficiency and the onset of control of the absorption process by slow transport of hydrogen into the alloy. For Pd-containing materials, Fukuzuka et al. (1980) showed that proton reduction was observed at much lower applied potentials on Pd-containing alloys than on Ti-2 and that there was a distinct correlation between alloy corrosion rate and H absorption rate in boiling HCl, Figure A3. The mechanism of H^+ reduction is well known to follow three distinct steps, and a fourth step can be added to represent absorption of hydrogen into the metal;

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[1] The efficiency of hydrogen absorption is defined as that fraction of the applied electrochemical current which leads to hydrogen absorption.

$H^{+} + e \circledR H_{ads}$	proton discharge
$H_{ads} + H_{ads} \circledR H_2$	recombination
$H^{+} + H_{ads} + e \circledR H_2$	electrochemical desorption
$H_{ads} \circledR H_{abs}$	absorption

For proton reduction on Ti-2, a Tafel slope of > 120 mV^{-1} is obtained. Such a slope, and the observation of a discharge threshold potential of ~ -0.6 V (vs SCE), is consistent with rate control by the proton discharge step as expected on an oxide surface; i.e. a surface without the catalytic properties to accelerate this first step.

As discussed in the main body of the text, and illustrated in Figure 12, the threshold represents the potential at which redox transformations ($Ti^{4+} \rightarrow Ti^{3+}$) occur in the oxide, thereby rendering it sufficiently conductive to support an interfacial electrochemical process. For the Pd-containing materials (Ti-1Pd and Ti-0.15Pd (i.e., Ti-7)), proton reduction occurs at much lower potentials and with much smaller Tafel slopes. (50 – 65 mV^{-1}). A slope in this range indicates control of the overall proton reduction reaction by the electrochemical desorption step consistent with the catalytic behaviour observed on noble metals such as Pd (Greef et al. 1985). This observation of catalyzed proton reduction at less negative potentials is clear evidence that the need for redox transformations in the oxide is not a prerequisite for proton absorption into the metal matrix. The behaviour observed is consistent with the existence of intermetallics, rich in noble metal content, which can function as "hydrogen windows" in the oxide.

Schutz and Xiao (1993) observed similar effects for proton reduction on Ti-2, Ti-7, and Ti-16, although no threshold value was identified. The Tafel slope for Ti-16 (100 mV^{-1}) was larger than that obtained for Ti-7 (80 mV^{-1}) indicating that the ability to catalyze proton reduction decreases as the Pd content of the titanium decreases.

This is consistent with the observation of Fukuzuka et al. (1980), that the efficiency of H absorption into the Ti also decreases with decreasing Pd content (Figure A3). As shown in the figure, the difference in measured absorption efficiency between Ti-2 and Ti-7 is less than a factor of 5 over the measured region. An even lower difference would be expected between Ti-2 and Ti-16.

Our own cathodic polarization studies on Ti-2, Ti-12 and Ti-16 specimens have shown interesting differences in the hydrogen absorption behaviour of these alloys. Figure A4 shows cathodic polarization curves recorded potentiostatically on Ti-2 in 0.27 $mol \cdot L^{-1}$ NaCl (pH ~ 1) at 95°C (Noël et al. 1996). In a separate set of experiments, the amount of hydrogen absorbed as a function of applied potential was measured. The hydrogen absorption behaviour can be separated into two distinct regions, denoted A and B on the figure. In region A (> -0.6 V) no hydrogen absorption into the metal was observed, while for more negative potentials in region B it was. This observation is consistent with the demonstrated existence of a hydrogen absorption threshold at (~ -0.6 V) (Murai et al. 1977) discussed above (Figure 11).

For Ti-12, absorption was observed at more positive potentials than -0.6 V consistent with the presence of hydrogen absorption windows which allow absorption before redox transformations occur in the oxide. In view of the results of Fukuzuka et al. (1980) for Ti-1Pd and Ti-7, we would have anticipated similar behaviour for Ti-16. However, no absorption of hydrogen into the metal was observed until E was < -1.0 V (vs. SCE). This observation was even more baffling since microscopic examination of the Ti-16 revealed the existence of a large number of randomly dispersed intermetallic particles, suggesting the separation of Pd into catalytic cathodes (Noël 1999) (Figure A5).

A hypothesis advanced by Ikeda (private communication) is that the intermetallic particles act as point conductors within an insulating TiO_2 oxide. At cathodic potentials the low resistance to current flow at these sites prevents polarization of the surrounding oxide, and the potential at the intermetallic must reach -1.0 V before a potential of -0.6 V becomes applied across the oxide. For this situation to prevent H absorption into the alloy, the cathodic intermetallics must either be unable to absorb H or capable of saturating with H and rapidly forcing its absorption efficiency to zero. If behaving in the latter mode the intermetallics would be acting as hydrogen storage sites which in the absence of any b-phase in the bulk of the alloy retain the hydrogen at the surface of the alloy. Since they are small and few in number their hydrogen content may be undetectable by bulk analyses.

To date, the nature and properties of these intermetallics present in Ti-16 have not been elucidated. According to the phase diagram for Ti-Pd, a Pd content of 0.05 wt.% is insufficient to exceed the Pd solubility and, hence, to cause phase separation as an intermetallic. This appeared to be confirmed by Kitayama et al. (1990) who showed that Ti-16 had a large grained equiaxed microstructure containing no separated intermetallics. However, when 0.3 wt.% Co was added to the alloy, a much smaller grained equiaxed structure containing a fine dispersion of particulates was obtained. The presence of these particulates, assumed to be Ti_xCo, led to further increases in the alloy's resistance to corrosion in hot reducing acid solutions.

The Ti-16 specimens used in impedance experiments (see Appendix B, Figure B2) and cathodic polarization/hydrogen absorption experiments (Figure A4) contained ~0.1 wt.% Fe, a concentration in excess of the ~0.03 wt.% solubility limit above which Watanabe et al. (1988) showed Ti_xFe particles precipitated. As discussed in Appendix B, Ti_xFe would be a reactive intermediate and expected to behave in a manner similar to that observed for Ti_2Ni in Ti-12. However, the impedance results, discussed in Appendix B, clearly show the intermetallic precipitates present in Ti-16 to be inert.

Two alternative explanations appear possible. The particulates could be Ti_xFe and simply difficult to activate for hydrogen absorption as discussed by Wu (1984). This would not account for their inertness at temperatures (> 65°C), when they would be expected to be reactive. Alternatively, the co-separation of Pd to yield a TiPdFe intermetallic particle could explain both their inertness and their ability to function as catalytic cathodes without causing significant H absorption. To function in this last manner they would have to act as hydrogen-saturated storage alloys with zero efficiency for the absorption of further hydrogen once saturated. Presently, no experimental evidence exists to evaluate these possibilities.

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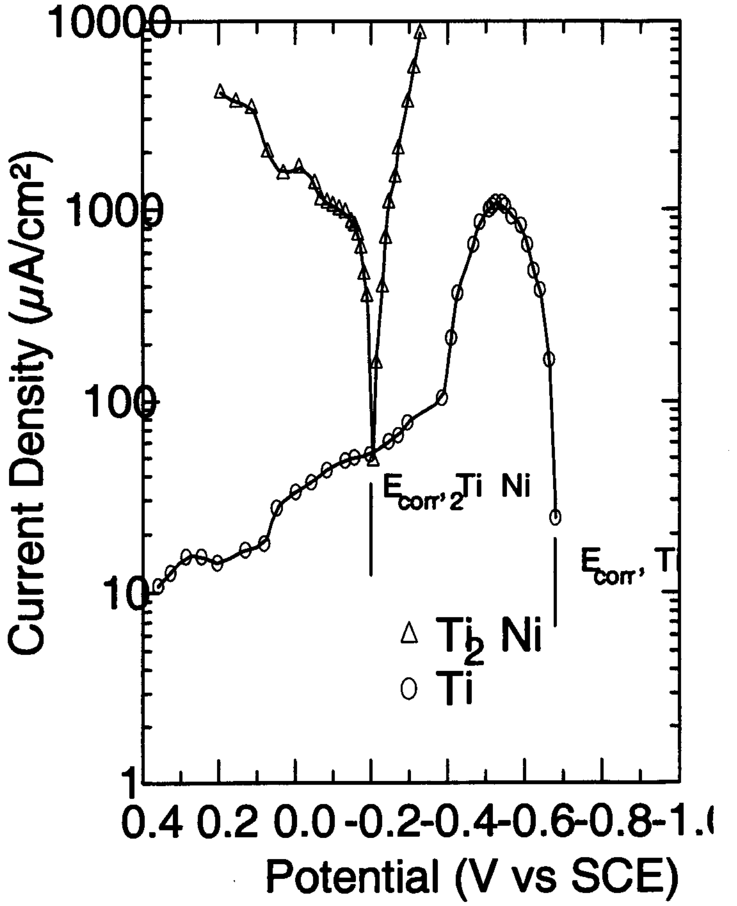

Figure A1: Polarization Curves Recorded (Separately) for Commercially-Pure Ti (o, Ti-2) and the Intermetallic Compound Ti_2Ni (Open Triangle) in Boiling Deaerated 1M HCl (from Glass 1983)

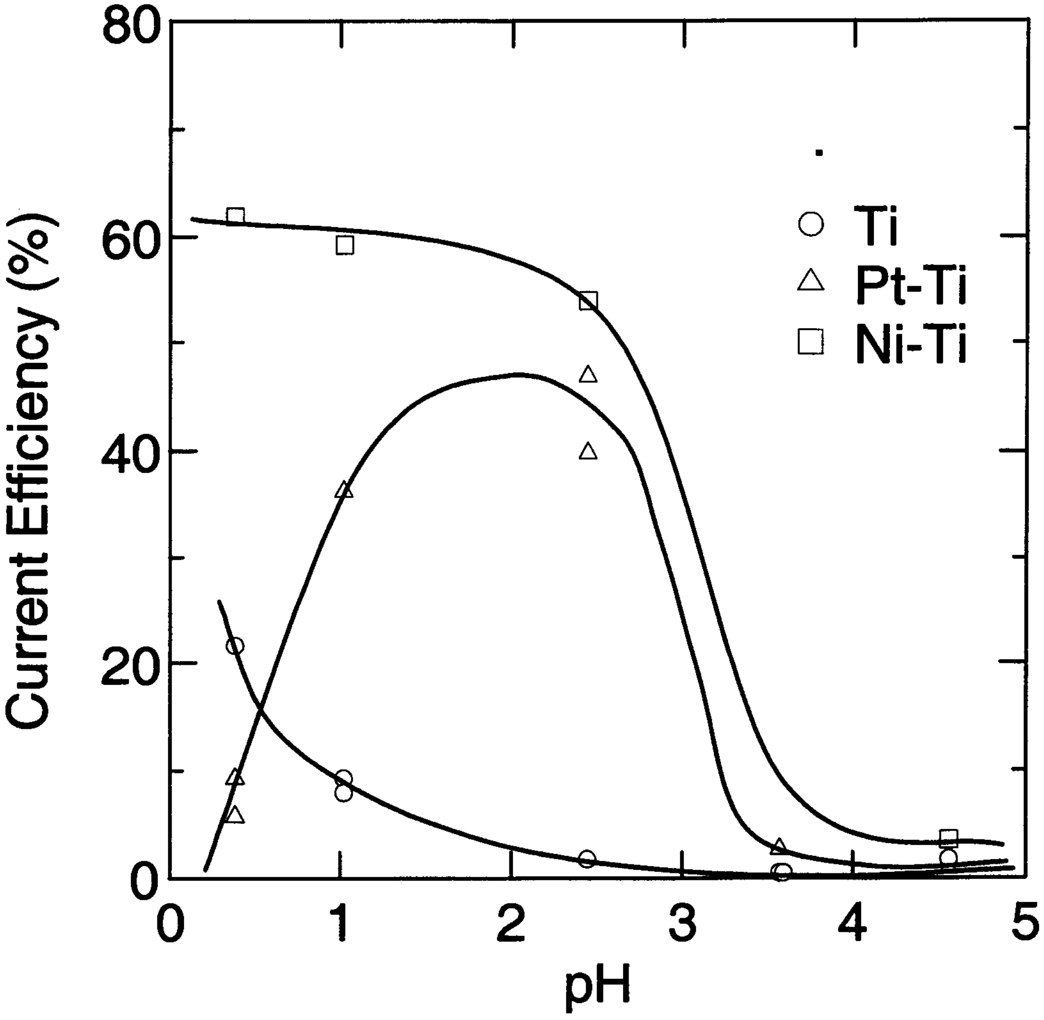

Figure A2: Effect of pH on the Current Efficiency for Hydrogen Absorption by Ti (Circle), Ni-Modified Ti (Square) and Pt-Modified Ti (Triangle) Recorded Galvanostatically at a Current Density of 0.5 mA·cm^{-2} at 25°C for 2 Hours (from Okada 1983)

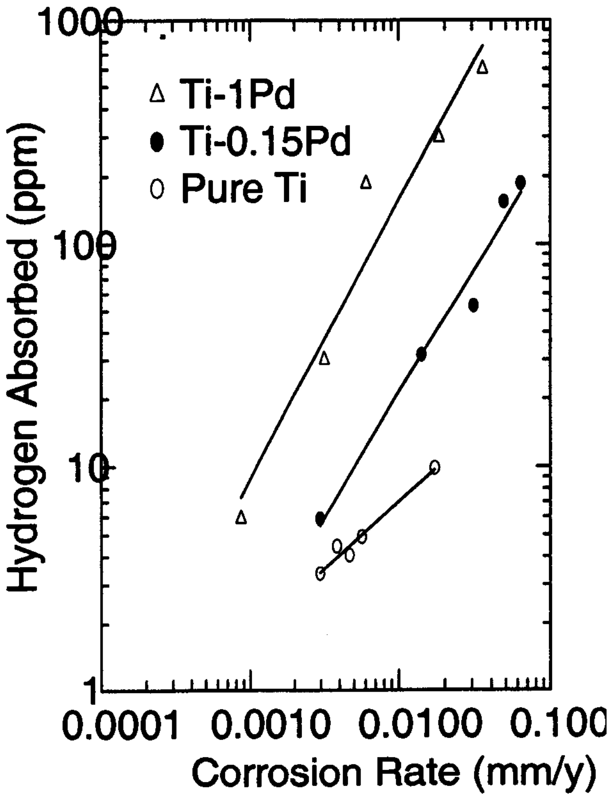

Figure A3: Relationship Between the Amount of Hydrogen Absorbed and the Corrosion Rate of Ti (Open Circle) and Titanium Containing 1% Pd (Triangle) and 0.15% Pd (Filled Circle) (from Fukuzuka et al. 1980)

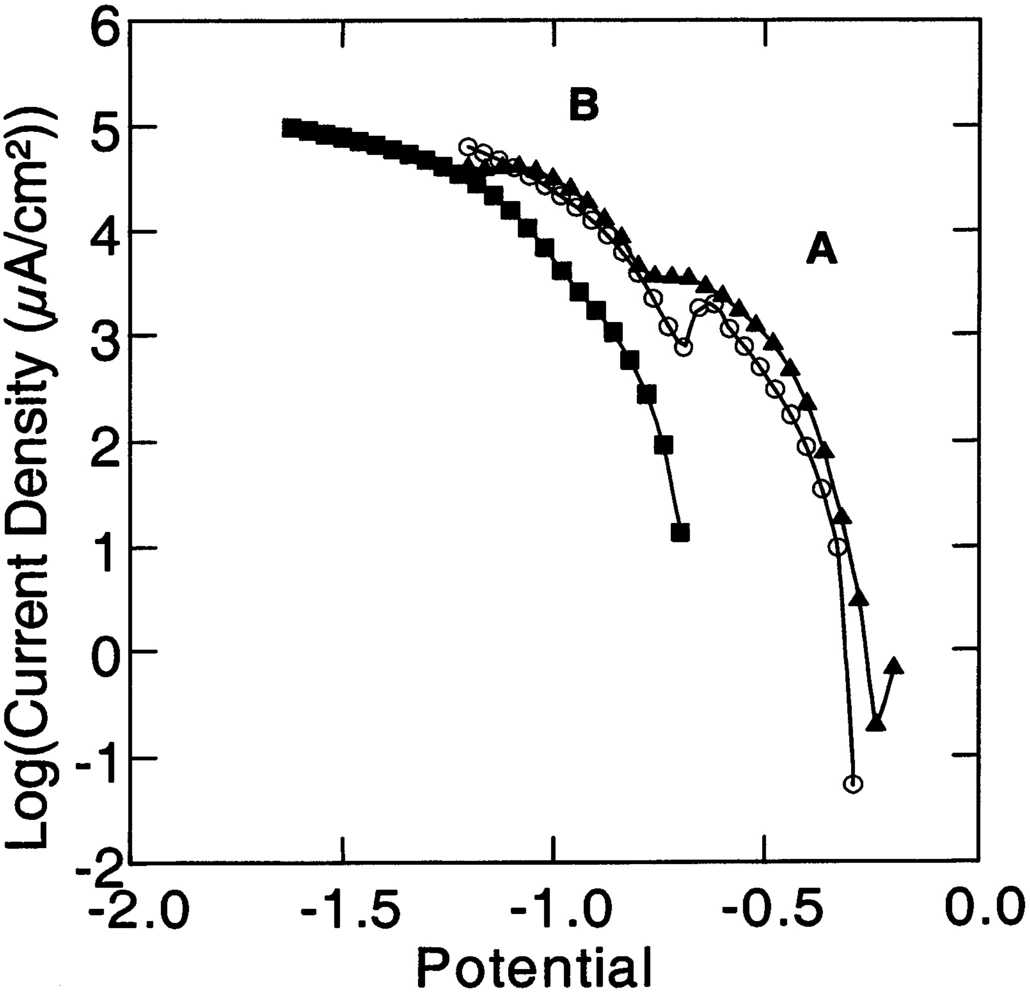

Figure A4: Potentiostatically Recorded Polarization Curves for Ti-2 in 0.1 mol·L^{-1} HCl + 0.27 mol·L^{-1} NaCl at 95°C. The curves denoted by the symbols open triangles and circles correspond to polarization curves recorded after an open-circuit transient in which the potential (E_{oc}) initially shifted to negative values before reclimbing to ~ -0.3 V. The curve denoted by the filled square symbol was recorded after E_{oc} fell to negative values (~ -0.6 V) and did not subsequently reclimb. A and B indicate the two segments of the polarization curves discussed in the text (from Noël et al. 1996).

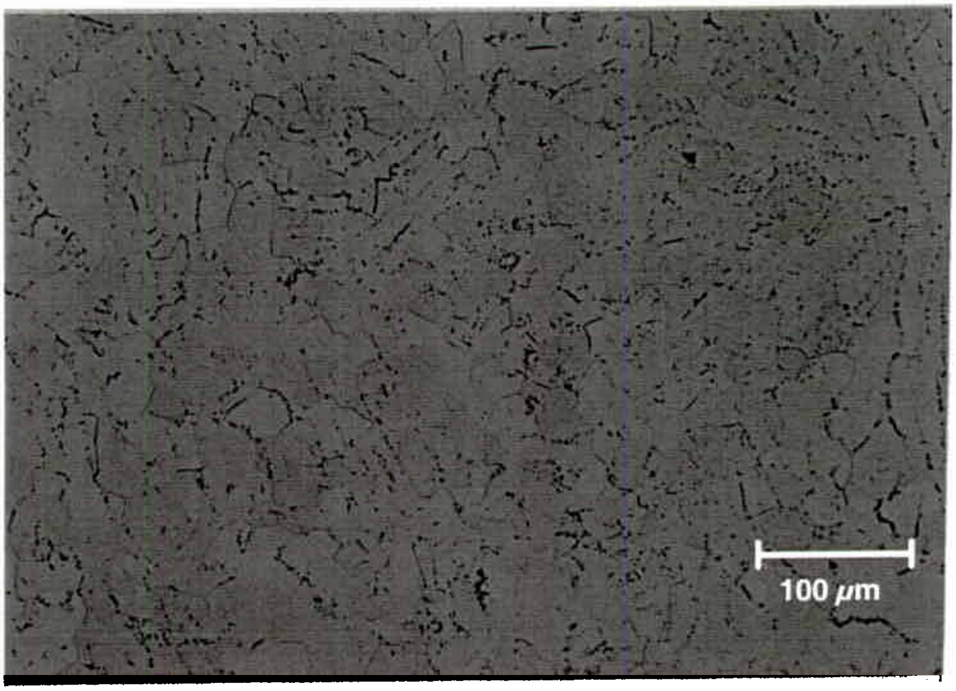

Figure A5: Photomicrograph Showing the Large Number of Randomly Dispersed Intermetallic Particles in Ti-16 (from Noël 1999)

APPENDIX B:

THE BEHAVIOUR OF THE ALLOYING ELEMENTS AND THE KEY IMPURITY, Fe, IN Ti-2, Ti-12 AND Ti-16

In an attempt to understand the properties of these alloys, in particular the properties of those sites at which the oxide film may be breached and hydrogen absorbed, we undertook an impedance study of a series of titanium alloys, including Ti-2, Ti-12 and Ti-16 in neutral 0.27 $mol \cdot L^{-1}$ NaCl as a function of temperature (ambient to 80°C) (Shoesmith et al. 1997, Noël 1999). For Ti-2, the impedance behaviour as a function of temperature showed a decrease in film resistance for $T > 65°C$, and could be interpreted in terms of a simple equivalent circuit of a parallel combination of a capacitor and a resistance (i.e., a single time constant circuit). The decrease in film resistance as the temperature increases is consistent with the film breakdown/ recrystallization process known to occur for $T > 65°C$ (Shoesmith and Ikeda 1997). The absence of a second time constant in the impedance response indicates that this breakdown is general, e.g. the generation of many lower resistance pathways at grain boundaries in the recrystallized oxide, and not the formation of discrete breakdown sites.

For the Ti-12 and Ti-16 alloys, however, the impedance results fit a model in which it is assumed that pores (or cracks and other faults) existed in the passive oxide film protecting the alloy. These faults were modeled using an equivalent circuit comprising an interfacial impedance (Z_i) in series with a pore resistance (R_{PORE}) both in parallel with a capacitance used to represent the properties of the passive film on non-faulted sites in the oxide (Figure B1). This model fitted the experimental data very well as discussed in detail elsewhere (Shoesmith et al. 1997, Noël 1999). The calculated values of the interfacial resistance (the resistive component of Z_I which comprises a parallel combination of this resistance and a double layer capacitance), taken to be the polarization resistance (R_p) at the base of the pore, and the pore resistance are plotted in Figures B2A and B2B. For Ti-12, the polarization resistance decreases with temperature, especially above ~ 65°C. By contrast no significant drop in polarization resistance is observed for Ti-16 up to 80°C. For both alloys the pore resistance (R_{PORE}) decreases slightly with an increase in temperature, but the absolute values for Ti-16 are about an order of magnitude lower than those for Ti-12.

A rational conclusion from these results is that, as the temperature increases, Ti-12 develops reactive sites (low z_i) at the bottom of relatively narrow, highly resistive pores (high R_{PORE}). By contrast, the sites at the bottom of relatively open pores/faults (low R_{PORE}) in Ti-16 remain inert (high Z_i) over the whole temperature range. A model based on the presence of "open" pores in Ti-16 is consistent with the photomicrograph in Figure A5. From the impedance results we would conclude that these particles are inert. For Ti-12, however, it is more reasonable to conclude that exposed sites within the passive oxide are reactive and that these sites coincide with the location of Ti_2Ni intermetallic particles or reactive b-phase in the underlying predominantly a-Ti matrix.

In support of this argument that the Ti_2Ni intermetallics in Ti-12 will be reactive if acidic conditions can be established are the results of Glass (1983) who has clearly shown in polarization experiments (Figure A1), that Ti_2Ni is very reactive in hot acidic solutions. His polarization curves show that, not only is Ti_2Ni a good catalyst for proton reduction, but that it also does not passivate when anodically polarized and hence is susceptible to rapid corrosion under acidic conditions. A similar susceptibility to corrosion has been demonstrated for b-phase Ti when its Ni content is high (Hall et al. 1985).

We would conclude from this evidence that it is possible for hydrogen absorption into Ti-12 to be facilitated by the coexistence of anodes and cathodes located at Ti_2Ni or Ni-containing b-phase at imperfections in the passive TiO_2 film. In the situation analyzed in impedance experiments this acidity will be localized at the film breakdown sites which appear in the oxide as the temperature increases. As within any occluded site a combination of metal dissolution, dissolved cation hydrolysis and limited transport would yield acidity.

Since the solubility of hydrogen in Ti_2Ni, and to a lesser degree the b-phase, will be substantially higher than in the a-phase it would be expected that this reactivity would enhance hydrogen absorption into the titanium matrix. An additional feature of the Ti-12 which would aid this process is the presence of b-phase which tends to occur as ligaments along the a-Ti grain boundaries (Glass 1983). This geometry, coupled with the higher diffusion rate of H in the b-phase (reported to be 10^5 times that in the a-phase (Wang et al. 1999)) would facilitate the transport of H into the bulk of the alloy (Figure 16).

The most common impurity in titanium alloys with the potential to exert a major influence on H absorption behaviour is Fe. Many studies of the influence of Fe on the corrosion of, and hydrogen absorption by, Ti have been undertaken with conflicting results (Cotton 1970, Covington and Schutz 1981, Schutz et al. 1984). Of particular interest in the present context is the ability of Fe-containing phases and intermetallic particles to absorb hydrogen. The influence of Fe would be expected to be similar to that of Ni in Ti-12, since it can both separate into intermetallic precipitates and stabilize the b-phase. It is likely that many of the inconsistencies for the influence of Fe on Ti corrosion can be attributed to variations in its distribution within the metal matrix.

Cotton (1970) clearly showed that H more rapidly diffused in Ti-2 as the Fe content was increased from 0.05 wt.% to 0.12 wt.%. This observation would be consistent with an increase in the b-phase content of the alloy with increasing Fe content. These results appear to be at odds with those of Covington and Schutz (1981) which showed that, for cathodic charging conditions ($9.6\ mA\cdot cm^{-2}$ in 1% NaCl (pH = 1) at 90°C) the efficiency of H absorption decreased from ~ 30% for [Fe] < 0.04 wt.% to ~ 15% for [Fe] > 0.20%. While no attempt to explain this apparent inconsistency was offered, it is likely that the decreased efficiency can be attributed to the separation of the Fe into Ti_xFe intermetallic precipitates at the higher Fe contents. A number of authors (Wu 1984, Ikeda et al. 1990, Watanabe et al. 1988) have clearly shown that as the Fe content of Ti-2 increases the a-grain size decreases and Ti_xFe intermetallics are formed. According to Watanabe et al. (1988) this occurs once [Fe] is > 350 $\mu g/g$ (0.035 wt.%).

While the intermetallic Ti_xFe has been shown to be a hydrogen absorber, it is claimed to be difficult to activate for hydrogen storage (Wu 1984). Hence, despite its presence at higher Fe contents it could actually impede hydrogen absorption despite acting as a H^+ reduction catalyst. According to Wu, the hydride formed on this intermetallic possesses less lattice distortion than that formed on a-Ti, a feature which would retard the diffusion of hydrogen. Similar speculations have been offered by Schutz et al. (1984). Such mechanistic features would lead to decreased H absorption with increasing Fe content.

That Fe present in b-phase leads to enhanced susceptibility to corrosion has been demonstrated by Ikeda et al. (1994) for Ti-2 and by Ruppen et al. (1983) for Ti-12. In both cases it appeared that if the Fe were located in b-phase it led to an increase in anodic current, and in corrosion experiments, an increase in corrosion current. However, when separated into Ti_xFe intermetallics, corrosion rates decreased and passivity was easier to maintain.

From these results it is clear that the distribution and local concentration of the alloying element Ni and the impurity element Fe will have a major influence on both the corrosion behaviour of Ti-12 (containing both Ni and Fe) and Ti-2 (similarly contaminated with Fe) and their ability to absorb hydrogen. Both Ni and Fe containing b-phase and Ti_2Ni and Ti_xFe intermetallic particles are susceptible to anodic dissolution in acidic environments. While it remains to be demonstrated whether Ni/Fe b-phase can also act as catalytic cathodes, there is little doubt in the case of the intermetallics, or in their ability to absorb hydrogen. It is likely, however, that absorbed H would remain localized at the intermetallic site unless the predominantly a-phase alloy contains b-phase ligaments which enhance transport of hydrogen into the bulk of the alloy. In the absence of these transport pathways the intermetallic particles may become saturated in H, a condition for which the efficiency of further H absorption approaches zero.

For the Ti-16 alloy, the presence of Pd in intermetallic particles would be expected to provide hydrogen absorption "windows", thereby allowing hydrogen absorption to occur at potentials less than the -0.6 V required to induce the redox transformations in the oxide and render it permeable to hydrogen. While the H absorption efficiency has been shown to decrease as the Pd content decreases (Fukuzuka et al. 1980, Figure A3) it was still surprising to discover that the absorption of H into this alloy was undetectable until potentials > -1.0 V.

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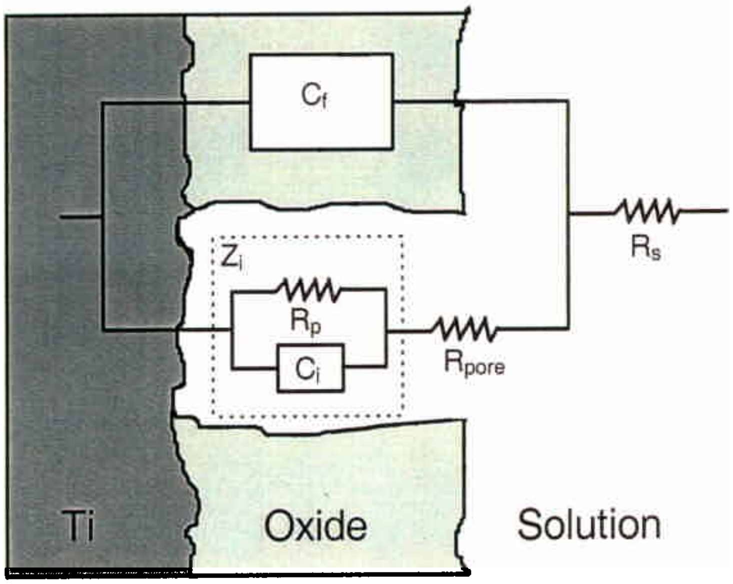

Figure B1: Equivalent Circuit Used to Analyze the Electrochemical Impedance Spectroscopy Data for Ti-12 and Ti-16

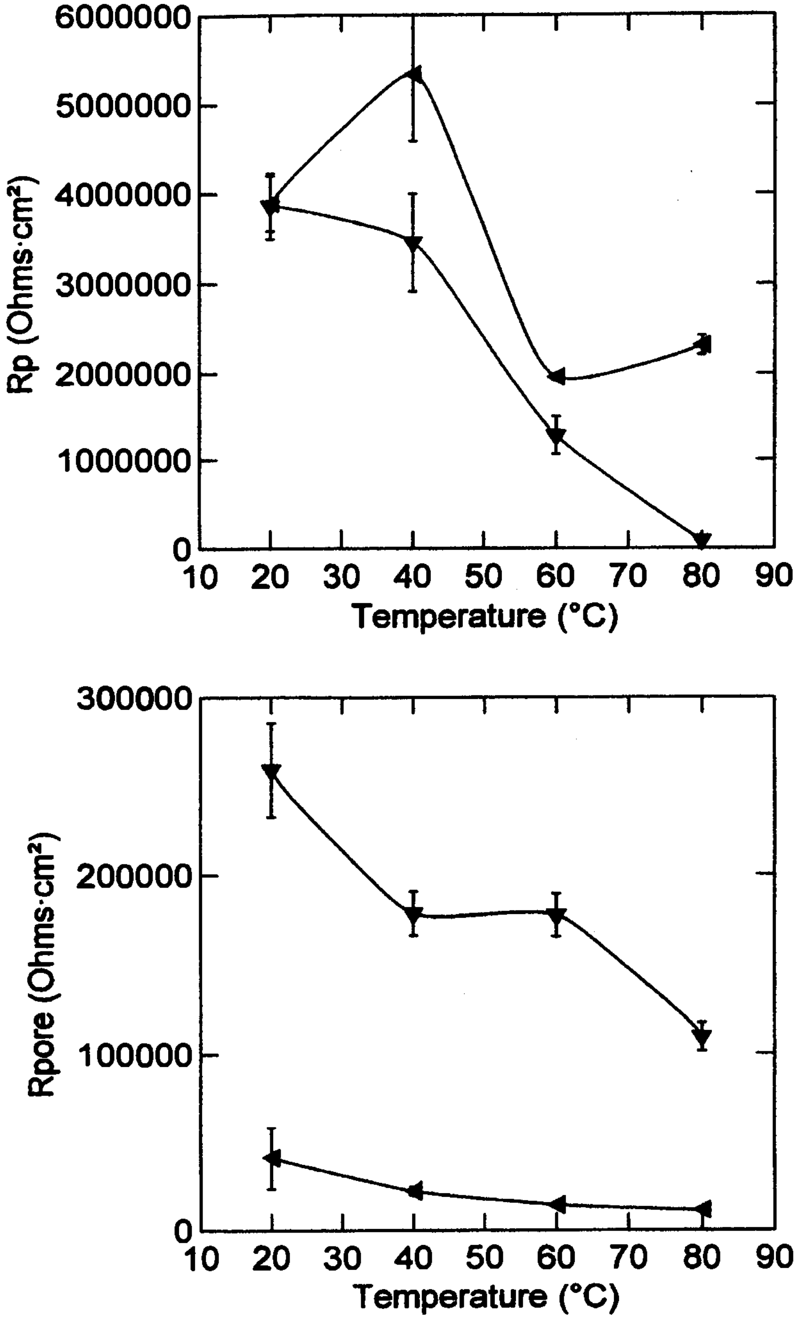

Figure B2: The Calculated Values of the Interfacial Resistance, R_p, (the Resistive Component of Z_I (Figure B1) Which Comprises a Parallel Combination of This Resistance and a Double Layer Capacitance) and the Pore Resistance, R_{PORE} (Figure B1), as Functions of Temperature for Ti-12 (Triangle) and Ti-16 (Tilted Triangle). The impedance data were recorded in 0.27 mol·L^{-1} NaCl after 24 hours on open circuit.

APPENDIX C:

THE CORROSION OF TITANIUM ALLOYS WHEN EMPLOYED AS A DRIP SHIELD

Since the initial writing of this report, a number of alternative waste package and repository drift designs have been considered. The primary alternative to the triple wall design is a dual wall waste package covered by a thick drip shield, itself then buried in backfill. It is proposed that the waste package be fabricated from an inner structural barrier of 316L stainless steel (5 cm thick) with an outer corrosion resistant barrier of Alloy-22 (2 cm thick). The drip shield (1-3 cm thick) would be fabricated from Ti-7 and Ti-16. If these packages are then emplaced using the enhanced alternative repository design (EDA II), they would be placed closer together within more widely spaced drifts than previously planned (See "Enhanced Design Alternative (EDA) II: Description and Plans for Refinement ", R.Dulin; presentation to the Mined Geologic Disposal Systems Board, July 21 (1999), Las Vegas).

This redesign would have a number of implications for the corrosion behaviour of titanium. The risk of localized corrosion, possibly enhanced by galvanic coupling, within an acidified dissimilar metal crevice would no longer be an issue. Of more concern would be the possibility of moist vapour corrosion and the potential for underdeposit corrosion under hot saline conditions. With the Ti separated from the other materials and used as a drip shield, the most corrosive environment would be that developed by the sequence of wetting and evaporative processes induced by seepage drips. The two most likely sites for the development of such an environment are under a salt deposit formed on the Ti surface at the interface between the drip shield and the backfill and at the base of the shield in contact with the floor of the drift.

Experiments and calculations presently underway (F. Wang, "Concentrated Corrosive Solutions Produced by Boiling Simulated Yucca Mountain Groundwater") suggest that aqueous conditions could be established for $T \leq 120^{\circ}C$. The worst aqueous environment anticipated (calculations are on going and further developments are expected) would contain approximately 10% chloride, 10% nitrate, 6% carbonate, 1% sulphate and 0.1% fluoride. The dominant cation would be sodium and the pH could be between 10 and 12, although even more alkaline conditions appear feasible. The boiling point for such a solution would be between 110 and 115°C.

CORROSION UNDER AQUEOUS VAPOUR CONDITIONS

The great majority of the drip shield surface, including the underside separated from the waste package by an air gap, is expected to experience only aqueous vapour conditions. Such conditions would not be expected to be corrosive to Ti alloys. As a consequence of the reduced spacing between packages in the EDA (II) repository design, temperatures > 200°C may be encountered initially and temperatures in excess of 100°C could persist for a few thousand years. Exact values will depend on ventilation and backfilling scenarios and schedules. However, at these high temperatures vapour should be expelled from the drifts and low humidity conditions maintained. The conditions anticipated at the Ti drip shield surface are not significantly different to those for the triple wall design. The available evidence on Ti corrosion in aqueous vapours was discussed in detail in Section 3.1.

CORROSION UNDER AQUEOUS CONDITIONS

Aqueous conditions, once established on the drip shield surface are expected to be extremely saline with a significant [F⁻] (0.1 wt.%) and a pH approaching, or even, exceeding 12. In the absence of the possibility of acidification within mixed metal crevices, as anticipated for the triple wall design, alkaline conditions would be expected to persist. Consequently, the primary concern is that a combination of enhanced passive corrosion, under alkaline conditions, accompanied by hydrogen absorption at those sites exposed to seepage drips will eventually lead to failure, with the most likely cause of failure being HIC or embrittlement. The prospects for the initiation of crevice corrosion are extremely remote with the proposed alloys of fabrication, Ti-16 and Ti-7.

Under general corrosion conditions, especially in the presence of oxygen as expected at Yucca Mountain, the maintenance of passive conditions would be expected to be reflected in positive corrosion potentials at the titanium surface. This, we would anticipate, would preclude significant hydrogen absorption which is more likely to occur under anoxic conditions at more negative potentials. Such anoxic aqueous conditions are not anticipated at Yucca Mountain. In the early stages of vault lifetime, when temperatures are high, the oxygen content of the vault will be low, but so will the water content, the only significant potential source of hydrogen (by reaction with Ti). Eventually, oxidizing conditions will be established and an open circuit corrosion potential, too positive to allow the redox transformations in the oxide required for the film to become permeable to hydrogen will be established. Also, for oxidizing conditions, any exposed noble metal intermetallic particles in the alloy should be passivated by a surface oxide film, and their catalytic properties for hydrogen reduction and absorption reduced.

However, the possibility of localized anoxic conditions associated with deposits are a possibility and the prospects of enhanced passive corrosion, driven by water reduction and accompanied by hydrogen absorption, may be feasible. Evidence is available in the published literature to clearly indicate that the passive corrosion rate of Ti (i.e., the TiO_2 chemical dissolution rate) will increase as the alkaline extreme is approached (Blackwood et al. 1988). Also, the industrial guidelines warn that there is a potential for hydrogen absorption providing the pH is sufficiently alkaline and the temperature high enough (Schutz and Thomas 1987).

Comparisons of the rate of passive oxide film thickening on commercially pure Ti (equivalent to Ti-2) in acidic, neutral and alkaline solutions showed that the film achieved a steady-state thickness and corrosion potential (~ -0.38V (vs SCE)) in 0.5N NaOH, but continued to thicken in neutral solutions, a process accompanied by a general shift of the corrosion potential to much more positive values (~ + 0.2V) (El-Basiouny and Mazhar 1982). The film thickness achieved in alkaline solutions was intermediate between those in acidic and neutral solutions. The observance of a steady-state thickness indicates that, as in acidic solutions, the rate of film formation at the metal/oxide interface is counterbalanced by its rate of dissolution at the oxide/solution interface.

Blackwood et al. (1988) measured the rate of dissolution of the passive film in 1.0 mol./L KOH (45°C) and found it to be about 3 nm/h (≡ 26 μm/y). This is comparable to the rate in 3 mol/L

H_2SO_4 (2.23 nm/h). If the same pH dependence prevails in alkaline as in acidic solutions, then this rate would fall by about an order of magnitude for each unit decrease in pH. Available results suggest the presence of F^- will not exert a major influence on the passive corrosion rate in alkaline solutions, although the evidence cannot be considered totally conclusive. Experiments on dental alloys (Reclaru and Meyer 1988) and in flue gas scrubber environments (Thomas and Bomberger 1983, Schutz and Grauman 1986) indicate no influence of F^- for pH ≥ 3.5, and XPS evidence on passive Ti specimens at high pH shows no incorporation of F^- into the passive film. A more extensive discussion of the effects of F^- was given in the main body of the text.

While clearly indicating that passive corrosion rates increase in alkaline solutions, the above evidence does not clarify whether the films themselves are more or less likely to be permeable to hydrogen than they are in neutral and acidic solutions. Voltammetric experiments in 1.0 mol/L NaOH indicate that the redox transformation in the oxide ($Ti^{IV} \rightarrow Ti^{III}$), necessary for hydrogen absorption to occur and for the oxide to become permeable to hydrogen transport, commences for $E \leq -0.6V$ (vs SCE) (Baez et al. 1992). This is approximately the same as in neutral solutions . This would suggest the transformation is determined by the solid state oxide properties and is independent of the oxide/solution interfacial properties. The former would be expected to be independent, the latter dependent, on pH.

Since the corrosion potentials measured by El-Basiouny and Mazhar are more negative in alkaline than in neutral solutions, Ti is likely to approach more closely to this hydrogen threshold in alkaline compared to neutral solutions. Despite this greater probability of absorption, what evidence exists indicates that the absorption of hydrogen does not occur readily under alkaline conditions and that there are many features of the surface behaviour of Ti which will retard the process. Based on the industrial guidelines proposed by Schutz and Thomas (1987) (their Figure 31), if aqueous conditions can be achieved on the drip shield surface for T < 125°C, then a pH ≥ 13 would be required before significant hydrogen absorption could occur. If this temperature were lower, then pH > 14 would be required. More conservative limits of pH > 12 and T ≥ 80°C where proposed by Schutz (1986).

While valuable for normal industrial situations, these guidelines do not rule out the possibility that slow absorption could occur over extremely long exposure periods. The early evidence of Covington (1979) showed that the hydriding of Ti was difficult to achieve unless the surface was abraded or sandblasted, even when galvanically coupled to Al in boiling simulated seawater, or after attempts to cathodically charge at pH = 14. Absorption did occur in > 10% NaOH.

A more detailed study was performed by Phillips et al. (1974). They observed a decrease in the extent of hydrogen absorption with increasing pH and, over a 50 hour period, the amount absorbed for pH ≥ 10 was immeasurably small. However, if the surface was abraded then absorption was observed at pH = 14 (over a 24 hour period). For pickled and vacuum annealed specimens, no absorption was observed above pH ~ 8. Subsequent aging of abraded specimens prior to application of the galvanostatic charging current lead to a decrease in the absorption rate and prolonged aging removed any influence of abrading. An experiment conducted at pH = 13 on Ti-12 at an applied potential of –1.05V at 80°C showed no hydride formation (Lunde and Nyborg 1993).

Many features of the performance of Ti alloys in alkaline environments remain uninvestigated. The question of how alloying additions to Ti alloys will influence hydrogen absorption is unknown, although no enhancement of their catalytic ability to reduce protons and facilitate hydrogen absorption is likely under alkaline conditions. On the contrary, the passivation of noble metal intermetallics, and accompanied by a reduction in absorption efficiency could occur.

Other factors are also likely to impede hydrogen absorption under actual repository conditions. For example, thermal oxidation has been shown to suppress corrosion and impede hydrogen absorption (Covington and Schutz 1981, Nakamura et al. 1998). Generally, such inhibition is noted for films grown thermally for short periods of time at high temperatures (> 400°C). However, a similar retardation may be achievable for films grown over many hundreds of years at the lower temperatures (200°C to 100°C) expected in the waste repository. Lunde and Nyborg (1993) reported that hydrogen absorption was suppressed, but not eliminated, in hot seawater by the build-up of insoluble scale deposits.

Clearly, whether hydrogen absorption occurs under alkaline conditions is dependent on the pH, the temperature and the state of the surface. When observed in alkaline solutions, absorption has generally required cathodic charging and, to be significant, surface damage. While the latter will definitely occur on the drip shield the former will not. It can be concluded that the absorption of sufficient hydrogen to cause failure by HIC of the drip shield is unlikely. However, the possibility that some hydrogen will be absorbed cannot be ruled out. The process is most likely to occur under a deposit providing sufficiently alkaline conditions can be maintained at that site. According to the conservative industrial guidelines (Schutz 1986), a $\mathrm{pH} \geq 12$ for $T \geq 80^{\circ}\mathrm{C}$ would be sufficient. However, most available evidence indicates a higher pH value is necessary. Since the possibility of establishing an extremely high pH will decrease as repository temperatures fall, so will that of hydrogen absorption. A reasonable scenario would be to accept the conservative industrial guideline as a lower limit below which absorption should cease. This would mean that the "window of susceptibility" for absorption would be the period from ~125°C, the maximum temperature at which aqueous conditions could be established, to 80°C.

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