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**A TECHNIQUE FOR CHARACTERIZING CREVICE CORROSION
UNDER HYDROTHERMAL CONDITIONS***

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ABSTRACT

A technique was developed to monitor crevice corrosion of Grade-12 titanium in a high magnesium synthetic brine under hydrothermal conditions. The current between the cathode and anode, and the potential of the whole crevice assembly, provide information on the various stages of corrosion. Occasionally, the decoupled potential of the cathode and anode are measured to give supporting information about the crevice conditions. A parallel test is run on a specimen which has small wells to collect crevice solution whose pH is determined at room temperature.

The current/potential results show that the crevice corrosion incubation period for a Grade-12 titanium crevice formed between two Teflon plates is approximately two days at 150°C. Optical and SEM observations show that the corrosion starts as isolated pitting which spreads along the surface as shallow pits. The corrosion conditions change significantly as the TiO_2 corrosion product fills the crevice, and the rate of corrosion may be greatly reduced after several days. The rate of crevice corrosion of commercial purity (Grade-2) titanium under similar conditions is approximately three orders of magnitude higher. In this case, active dissolution of metal starts during the initial heating of the autoclave and the incubation period is negligible.

KEY WORDS

Crevice Corrosion, Hydrothermal, Titanium and alloys, Brine, Pitting, Electrochemical Techniques, Incubation Period.

INTRODUCTION

In the disposal of high level radioactive waste in a deep rock salt repository the metal container must retain its integrity for a period of 300-1000 years while the fission product nuclei decay to low levels. Titanium Grade-12 is a candidate container material which in high temperature brine is susceptible to corrosion and this material must be adequately characterized to determine its capability to withstand failure by corrosion for very extended times. Although commercially pure titanium is known to be susceptible to pitting and crevice corrosion in seawater and other chloride containing environments above room temperature,⁶⁻⁹ Grade-12 titanium was initially believed¹⁰ to be resistant to these types of corrosion. Lately, an investigation¹¹ at Brookhaven National Laboratory gave the first indication of crevice corrosion of Grade-12 titanium in brine at 150°C. Continuation of this work has confirmed the initial observation and determined that the severity of corrosion is enhanced when the brine solution is oxygenated. The corrosion product is found to be a mixture of anatase, rutile and lower oxides of titanium. In general, the extent of crevice corrosion of Grade-12 titanium is much less than that for Grade-2 titanium, and its presence may be limited to certain ranges of test conditions.

Usually the crevice corrosion of passive metals in a chloride solution is believed to proceed in four stages.¹⁻⁵ In the first stage, oxygen is consumed within the crevice at a faster rate than can be supplied from outside, thus forming an oxygen concentration cell. As the thickness of passive oxide film within the crevice increases, the potential of the metal rises. Slowly, the cathodic reaction is moved to the freely exposed external surface.

Subsequently, the pH decreases and the concentration of chloride ion within the crevice solution increases in order to maintain charge neutrality. During the third stage the crevice solution becomes sufficiently aggressive for the passive film to break down. In the final stage, the metal within the crevice continues to dissolve actively and crevice corrosion propagates in a self-sustaining manner.

This model of crevice corrosion is very general and details of the mechanisms for each stage may vary considerably from metal to metal. For example, Oldfield and Sutton³ have listed ten different categories of variables which determine the behavior of a particular crevice. Therefore, considering the complexity of a realistic crevice an experimental characterization of each stage is very important. Note, also, that the stages of crevice corrosion may be divided into two parts. There is an incubation period during which corrosion conditions develop within the crevice but no major loss of metal results, and there is a propagation period commencing with rapid corrosion in the crevice region.

In the past, several direct and indirect experimental methods have been developed to monitor various stages of crevice corrosion.¹²⁻²³ The direct methods^{12-15,18,22} use an artificial crevice and monitor its current or potential without disturbing the electrochemistry, whereas indirect methods make use of external electrochemical measurements. All of these methods have been developed for room temperature measurements and are, therefore, not suitable for simulating waste repository conditions of high temperature, high pressure and radiation, etc. However, very recently Taylor and Caramitas,²³ and Diegle⁹ have developed techniques suitable for testing under hydrothermal

conditions. The former technique monitors in situ crevice pH and potential, but not the current which is a simple measure of total corrosion. Also, in this case the crevice gap is too large for a Grade-12 titanium to attain active corrosion conditions. In the cell and specimen design due to Diegle, the current between the cathode and anode and the potential of the whole crevice assembly are monitored continuously to determine the end of incubation and onset of active corrosion. In the present work we have made use of the advantages of both of these methods as well as incorporating certain features to determine the final pH of the crevice solution. Also, a plane circular crevice geometry has been used to make future modeling of corrosion kinetics mathematically simple. For the purpose of comparison, results on a Grade-2 titanium crevice are also included. To support the predictions from electrochemical measurements, the surface and morphology of corroded specimens were extensively studied using optical and scanning electron microscopes. Presently, the experiments are conducted at 150°C in brines of different concentration and pH, but do not include any studies on the effect of irradiation on crevice corrosion.

EQUIPMENT DESIGN AND EXPERIMENTAL PROCEDURES .

Materials

The chemical compositions of Grade-12 and Grade-2 titanium sheets as supplied by the vendor are given in Table 1. A thicker sheet was used for pH measurements to provide sufficiently deep wells for crevice solution to be collected. Care was taken to avoid any galvanic corrosion of the test specimen which could arise from contact with a dissimilar metal.

The chemical composition of the test solution, commonly referred to as WIPP Brine A in the nuclear waste management literature, is given in Table 2. This is a high magnesium containing nearly saturated brine solution representative of one of the proposed sites for nuclear waste disposal in New Mexico.²⁴ To lower the pH of the solution appropriate amounts of HCl were added. To increase the dilution, doubly distilled water was added.

Cell Design

A schematic diagram of the autoclave assembly and the measuring equipment is shown in Figure 1(a). The bolted top of a one-gallon Type 316 stainless steel vessel (A) was modified to allow the access of a reference electrode (RE), a thermocouple (TC) and two leads which were connected to the cathode (CC) and crevice specimen (CS). In all cases insulated Conax type feed-through assemblies provided leak tight connections. The titanium lead wires were covered with Teflon for electrical insulation from the solution. An inlet near the top of the cylindrical surface of the autoclave was machined to connect a pressure gauge (PG), a safety rupture disk (RD) and a gas control valve (GV). An electrical furnace (H) with a temperature controller heated the autoclave to the desired temperature. To avoid corrosion of the autoclave, a Teflon liner (L) was used to isolate brine from the steel parts; the chromel-alumel thermocouple was encased in a titanium sheath.

The Ag/AgCl reference electrode (RE) consisted of a Teflon tube whose lower end provided a junction with the brine solution through a porous zirconia plug. The top end of the tube was maintained at room temperature. It was plugged with a silver wire which had a layer of AgCl deposited by electrolysis. The tube was filled with a saturated solution of potassium

chloride. Additional solid KCl was added to maintain saturation at elevated temperature, which was found to be necessary to prevent local boiling of the KCl under the test conditions used. The potential (vs Ag/AgCl) of the crevice assembly, consisting of a freely exposed cathode (CC) connected through a Keithley 150AR ammeter (A) to the anode (CS), was monitored with EG and G Model 173 potentiostat (V). The values of current and potential were recorded on strip chart recorders (R). A separate crevice assembly was used for pH measurements. It consisted of an anode specimen (PS) connected to a freely exposed cathode (PC), and this was placed at the bottom of the Teflon liner.

Specimen Preparation and Configuration

In the present tests the cathode and anode of a crevice assembly were physically separated. The cathode, both in the case of current or pH measurement assembly, was a polished 5-cm diameter circular disk. The anode part of the current-assembly is shown schematically in Figure 1(b). Here, the anode (CA) was a mirror polished disk sandwiched between two Teflon plates (TP) of the same diameter. Thus, the crevice was formed on both sides of the specimen and its area was equal to the total cathode area. A screw made of the same metal as the specimen was used to provide the electrical connection from the anode to the outside of the autoclave. The screw and the crevice were insulated from the test solution by an enamel layer (E). Only the edge of the specimen was freely exposed to the solution. Finally, a very narrow crevice was formed by tightening the titanium screws which pressed the Teflon disks under two larger titanium discs (PP1 and PP2). These disks were not polished and, therefore, could not form a corrosive crevice.

As shown schematically in Figure 1(c), the design of the anode part of the pH-assembly is essentially the same as that of the current-assembly. In this case, however, a thicker disk (PA) was used to provide small wells (W) of diameter 0.14 cm (one at the center and another near the edge) to collect crevice solution. Also, the electrical connection to the cathode was placed at the side and no enamel was used. The titanium pressure disks (PP1 and PP2) had partly open holes to accommodate titanium screws so that this assembly can be opened quickly even after quenching it to liquid nitrogen temperature.

Test Procedure

Before starting a test all the cathode and anode specimens were mirror polished and weighed to allow subsequent examination of the effects of crevice corrosion. The anode specimens were submerged in the test solution at room temperature and then assembled as shown in Figures 1(b) and 1(c). In this manner any uncertainty regarding the ingress of solution to the inside of the crevice was eliminated. The current-anode assembly was kept for one day under ambient conditions to cure the enamel. Before closing the autoclave the brine solution was saturated with oxygen by bubbling the gas through it for a minimum of one hour. Next, the electrical connections were made as shown in Figure 1(a) and the autoclave was kept under an oxygen pressure overnight to check for leaks in the system. This leak check became necessary due to the highly corrosive effects of brine on stainless steel components, as evidenced by stress corrosion cracking of the autoclave after several tests. If no leak was detected, the oxygen overpressure was reduced to atmospheric level and the autoclave was heated to the test temperature ($\sim 150^{\circ}\text{C}$). At this temperature, the equilibrium pressure of the brine solution was approximately 60 psig.

During the recording of current and potential the anode and cathode were coupled most of the time via the ammeter. Occasionally, the two electrodes were decoupled for a short time. After a few minutes the potential of the two electrodes reached stationary values which were recorded, and then the usual connections were restored.

The duration of a test at elevated temperature was typically two weeks. At the end of the test, to facilitate rapid cooling, the furnace around the autoclave was replaced by a bucket containing ice and water. When the temperature within the autoclave was below the boiling point of brine, an aliquot of the gases generated during corrosion was collected for chemical analysis by mass spectrometry. Then the autoclave was opened, and the pH-anode assembly was immediately quenched in liquid nitrogen to minimize any changes in the chemistry of crevice solution while disassembling the crevice. The pH was measured with a microcombination probe [Model MI-410, Microelectrodes Inc.] after the crevice solution in the wells had warmed up to room temperature. The tip of the pH probe required the well diameter to be larger than 1.2 mm. Some error in the pH measurements might have been incurred due to the condensation of atmospheric moisture.

Finally, all four anode and cathode specimens were ultrasonically cleaned three or four times in distilled water and weighed after drying. The anode specimens were examined under optical and scanning electron microscopes (SEM) to determine the morphology of crevice corrosion. The corrosion on Grade-12 titanium surfaces was in the form of pitting rather than uniform crevice corrosion. Therefore, some of the specimens were sectioned across the thickness at low cutting speeds and examined in an SEM to determine the shape of the pits.

For Grade-2 titanium, which showed extensive crevice attack, the corrosion product was also analyzed by X-ray powder methods.

RESULTS

Current and Potential Measurements

The time dependent variation of current from cathode to anode, and of potential of the coupled crevice assembly, as shown typically in Figure 2 for a Grade-12 titanium crevice in dilute Brine A (diluted from the composition given in Table 1 by a factor of 10) appears to be very complex. However, the behavior of all the tests shows the following common features:

- (a) In the beginning when the whole assembly is at room temperature, the crevice potential increases at a rate which decreases with time. During this period the current is essentially zero. Initially the uncoupled potential of the 'cathode' specimen is higher than that of the anode assembly, but this may be reversed at a later time.
- (b) During heating of the autoclave, which may take a few hours, a strong negative current accompanied by a sharp decrease in crevice potential is recorded.
- (c) As the temperature approaches the testing value, the current again becomes zero and the crevice potential shows an increase. At this stage the uncoupled potentials of the cathode and anode specimens are about the same. For approximately one day, as the temperature is kept constant, the current and potential values do not show any appreciable change.

- (d) In the next stage, the current shows an abrupt increase, usually as a spike which subsequently returns to a high positive value. The crevice potential, at the same time, shows an abrupt decrease. After this abrupt change, the uncoupled cathode potential remains at a much higher value than that of the anode assembly.
- (e) In the following period which covers most of the test time, the variation of current and potential does not show any reproducible pattern. However, on a positive background, many sharp peaks in current accompanied by decreases in potential are observed.

The general features described above for Grade-12 titanium crevices in dilute Brine A are also found for acidified undiluted Brine A (starting pH at room temperature = 4.2) - see Figure 3. Note that in this case, the current during the last few days of the test is reduced to a considerably lower value. In a similar test in neutral undiluted Brine A (results not shown), the crevice current was reduced to such low values at an even earlier time. Figure 3 shows that after 300 hours, although the difference between the uncoupled cathode and anode potentials does not change appreciably, the crevice current continues to decrease. This suggests an increasing resistance to the corrosion process. Also note that during this period the potential of the whole crevice assembly increases gradually.

The current/potential behavior of Grade-2 (commercially pure) titanium crevice in neutral Brine A is shown in Figure 4; the decoupled potentials were not measured in this case. This figure shows several important differences as compared to Grade-12 titanium crevices. Firstly, the crevice current is approximately three orders of magnitude higher. Although the behavior of the

crevice potential and current at room temperature is similar for both metals, the Grade-2 titanium crevice does not show any negative current during heating. Instead, the next stage of abrupt increase in current starts during heating. There are no further spike-like features. Finally, after about 125 hours the crevice current not only approaches zero, but changes polarity. Because of this unusual change of polarity, this experiment was terminated early.

Morphological Observations

The extensive corrosion of the current-anode specimen used in the Grade-2 titanium crevice is shown in Figure 5. Although the whole metal surface corroded, the attack was most severe near the edge. The loss of metal from an isolated area of the cathode specimen, an unusual feature, is shown in Figure 6. Otherwise, the cathode specimens developed a thin strongly adherent oxide film. The X-ray powder diffraction analysis of the anode corrosion product identifies it as mostly rutile, but a few lines could only be related to titanium hydride.

In the case of Grade-12 titanium crevices, the extent of corrosion was much less and the crevice gap appeared to be a critical parameter for the development of corrosive conditions within the crevice. Thus, a specimen corroded more or less uniformly (on a coarse macroscopic scale) if the crevice gap was small and uniform. The corrosion was much less in the areas containing relatively large volumes of the solution such as in the center of a specimen (Figure 7) or around the pH-wells (Figure 8).

An examination of the corroded surface under an optical microscope shows that corrosion starts in small isolated areas. During the early stages

(Figure 9) a pit is formed, which at a later stage becomes filled with a white corrosion product (Figure 10). This product has been identified as mostly rutile, although initial oxidation of titanium results in the formation of a protective layer of anatase. Transformation of titanium to rutile requires a 5.3% increase in volume. Thus, corrosion will produce large stresses in the crevice and the oxide prefers to grow in a direction which would accommodate such stresses. This is demonstrated in Figure 11 by the alignment of oxide covered pits along the scratches in the adjoining Teflon disk.

Figure 12 shows a vertical cross-section through a pit formed on a Grade-12 titanium crevice sample. As the metal corrodes, the oxide grows above (area A) as well as under (area B) the original surface of the specimen. Because of the constraints on oxide growth in the vertical direction, the pit tends to grow horizontally. For this reason most of the pits are found to be rather shallow. Area C in Figure 12 is also oxidized to some extent. Note that a large crack has been initiated in the pit region which propagates parallel to the crevice surface.

pH and Weight Measurements

In the initial experiments with Grade-12 titanium, the wells to collect crevice solution were 2.8 mm in diameter. Very little corrosion occurred in the vicinity of such large wells, and, therefore, the pH of the solution could not be considered representative of the crevice conditions. It was concluded that for crevice corrosion to occur in a Grade-12 titanium, the crevice volume should be very small. Therefore, in later experiments, the well diameter was reduced to 1.4 mm which was the minimum possible to use the pH probe. Even for a well of this size, in some cases (for example the central area in

Figure 8) much less corrosion occurred in its vicinity. Thus, the observed values of pH within a Grade-12 titanium crevice (listed in Table 3) may be considered as an upper estimate of the true value. In the case of dilute Brine A, the pH of condensed moisture in the uniformly corroded area was as low as 1.8. The condensed moisture outside the crevice had a pH of 5.9.

In all experiments with Grade-12 titanium, the weight of both current and pH anode specimens increased as a result of corrosion. The weight increase of the pH-anode (Table 3) was approximately one and a half times the increase for the current specimen. There are two possible reasons for this observation: (a) The freely exposed edge area of an anode acts as a cathode. This area, which contributes to the corrosion reaction, was appreciably larger for the thicker pH specimen; (b) The electrical resistance of the connecting path between cathode and anode was smaller for the pH assembly.

The weight increases for the cathode specimens were approximately two orders of magnitude smaller than for the anodes. The chemical analysis of the gas phase in the autoclave after the test showed large fractions of hydrogen (up to 60 mole percent). However, in these tests severe corrosion of the titanium screws was noticed and may be responsible for the generation of this gas.

In the case of the Grade-2 titanium crevice, the current anode was very severely corroded. After simple scraping, the specimen showed a 6.8% loss in its weight. Since all of the corrosion product could not be removed, the actual loss in weight was probably much larger.

DISCUSSION

The present electrochemical and pH measurement results for a Grade-12 titanium crevice in Brine A at 150°C are in general agreement with the usually accepted model of crevice corrosion according to which the corrosion proceeds with oxygen depletion, increase in proton and chloride ion concentration, breakdown of the passive film and then propagation by active dissolution. However, there are a few observations which point to additional details of the corrosion mechanism. With reference to Figure 2, we find that initially at room temperature the crevice potential increases due to more or less uniform growth of oxide film both inside and outside the crevice. In the very early stage of testing the anode specimen has been in contact with brine for a longer duration than the cathode and, therefore, has a thicker oxide film and higher potential. At a later time (the second and third sets of uncoupled potentials) the oxide film on cathode has grown thicker than that on the anode, but the temperature is too low to initiate the second stage of crevice corrosion and the current remains negligibly small. Next, during heating of the autoclave to the test temperature the crevice potential shows a sharp decrease in response to the equilibrium conditions at the higher temperature. The reason behind the negative corrosion current during this period is not clear. After reaching the test temperature (~150°C), the growth of oxide film both on the anode and cathode continues in a similar way to that at room temperature, but at a much faster rate. At the same time proton and chloride ion (as well as possibly some other anion) concentrations within the crevice change according to local potential, concentration gradients and the diffusion coefficient of the various species. The variation of crevice potential in

this time period is very complex and is determined by the contributions from all these sources. The current, however, remains very small, thus suggesting that the metal has not yet corroded significantly.

As the chemistry within the crevice becomes increasingly corrosive, the protective anatase film breaks down at least in parts of the crevice and fresh metal is exposed to the solution. The active dissolution of the metal (Figure 9) is characterized by a sudden increase in current and lowering of potential. This is the beginning of observable corrosion within the crevice. The ultimate corrosion product is porous rutile which presumably is formed via the hydrolysis of some type of titanium-chloride complex. The production of rutile fills the actively corroding pit (see Figure 10) and thus inhibits metal dissolution to some extent as shown by a decrease in current. Once the metal dissolution state has commenced, the cathode remains at a much higher potential than the anode. This observation of decoupled potentials is direct proof of separation of anodic and cathodic parts in the present design.

The irregular variation of current as well as physical examination of the crevice specimens (Figures 7 and 8) shows the inhomogeneous nature of corrosion within the crevice, probably due to the high sensitivity of crevice solution chemistry with respect to crevice gap size which may not have been constant throughout the crevice. The spikes in crevice current, which are always associated with lowering of potential, represent the onset of active dissolution in a new area within the crevice.

The extent of corrosion in a crevice is most simply determined from weight loss measurements. However, in the present case, such an approach will be very misleading for two reasons:

(a) The corrosion product, rutile, cannot be easily removed from the specimen surface and, therefore, we find a weight gain rather than a loss. However, the weight gain may not be a true measure of corrosion since some of the corrosion products may have dissolved in the solution. Since the extent of corrosion is proportional to the total flow of electrical charge between anode and cathode, a better estimate of crevice corrosion can be obtained from the area under the current-time curve. In this respect physical observations agree with the integrated current obtained from data such as those shown in Figures 2-4.

(b) The mechanism of crevice corrosion is found to start as pitting. From the point of view of containment of nuclear waste, the maximum penetration rather than average metal loss is important. However, microscopic observations show that these pits are rather shallow (Figure 12). Thus, as long as crevice corrosion occurs over the whole surface, the container penetration time can be roughly estimated if comprehensive experiments are conducted. A crevice specimen which corrodes uniformly will show less drastic changes in current (Figure 2) as compared to the one with big variations in current (Figure 3) which corresponds to isolated areas of corrosion.

From earlier crevice corrosion test data,²⁵ temperature has been shown to be a very important parameter, and no crevice corrosion in chloride-ion-containing environments is found at room temperatures. Therefore, to determine the incubation period in the present experiments we may assume the start of the incubation period to be when the crevice has just attained the test

temperature. The end of the period would correspond to the sudden jump in current thereafter. With this definition, the incubation periods are determined to be 68, 45 and 44 hours for the neutral, acidic, and dilute Brine A solutions, respectively. Within the uncertainty of the various experimental parameters these values are similar. We may, therefore, conclude that all three test solutions are equally corrosive as defined by the initiation time for active crevice corrosion. In the case of a Grade-2 titanium crevice the solution is so corrosive that the incubation period is essentially zero.

The shorter incubation period in the case of acidic Brine A is a result of the crevice solution reaching the critical acidity level earlier than it would for the neutral solution. However, it is not clear why for the 10-times diluted Brine A the incubation period is shorter than for normal Brine A which also shows lower total corrosion. One possible explanation is that the concentration of dissolved oxygen was higher in dilute brine, which caused early formation of an oxygen concentration cell.

An important observation from all of the present current vs time measurements is that the current decreases after a few days, and in some cases (Figure 3) it even approaches zero. Similar observations were made by Diegle⁹ on Grade-2 titanium crevices. This suggests that eventually the rate of crevice corrosion approaches a near-zero value. Such behavior is presumably due to the corrosion products (oxides, etc.) within the crevice. An increase in the crevice resistance is also evident from Figure 3 where at the end of the test the current is reduced to a very small value although the difference in cathode and anode potentials has not changed appreciably. Thus, if by some mechanism rate inhibiting corrosion products are removed, crevice attack will

be restarted.

Finally, a comment on the unusual observation of loss of metal from the Grade-2 titanium cathode (Figure 6) is warranted. Tomashov²⁶ has proposed this kind of observation of loss of cathode (in more aerated conditions) where an increase in aeration does not significantly alter the anodic process, but reduces cathodic polarization. Such a situation was probably reached in the present experiment after the corrosion of the anode specimen had been reduced greatly due to corrosion products, as also suggested by the negative current after approximately 130 hours (Figure 4). The presence of titanium hydride in the corrosion product is consistent with the observations by Griess⁷ who observed a large fraction of cathodic reaction to be a reduction of hydrogen.

CONCLUSIONS

By measuring the variation of current and potential with time, the experimental technique described above can be used to monitor the progress of crevice corrosion under hydrothermal conditions. The measurement of final pH of the crevice solution and of decoupled potentials of cathode and anode of the crevice assembly provide further information about the mechanisms of corrosion.

The results show that Grade-12 titanium is much less susceptible to crevice corrosion than Grade-2 titanium in Brine A at 150°C. Increasing the acidity of the brine solution to a pH = 4.2 or diluting it ten times has little effect on the incubation period. This suggests that the critical chloride concentration needed for the breakdown of passivity is already present in dilute Brine A.

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TABLE 1--Vendor supplied chemical analysis of Grade-12 and Grade-2 titanium.

	C	Fe	N	Mo	H	O	Ni	Ti
Grade-12 Titanium								
(Current specimen)	0.009	0.10	0.010	0.27	0.007	0.13	0.84	Balance
(pH specimen)	0.013	0.13	0.012	0.31	0.008	0.13	0.7	Balance
Grade-2 Titanium								
(Current specimen)	0.008	0.05	0.004		0.005	0.07		Balance

TABLE 2--Composition of WIPP Brine A.

Component	Concentration (ppm)
Na^+	42,000
K^+	30,000
Mg^{+2}	35,000
Ca^{+2}	600
Sr^{+2}	5
Cl^-	190,000
SO_4^{2-}	3,500
I^-	10
HCO_3^-	700
Br^-	400
BO_3^{3-}	1,200

TABLE 3--pH of the crevice solution and weight gain of the crevice anode
after two-week tests in three brines.

Bulk Solution	Crevice Solution pH	Weight Gain of pH Specimen (g/cm ²)
Neutral Brine A	3.2	7.0×10^{-4}
Acidic Brine A	3.8	9.5×10^{-4}
Dilute Brine A	2.8	12.3×10^{-4}

FIGURE CAPTIONS

1. Design of the testing equipment for crevice corrosion under hydrothermal conditions (diagram no. - scale). (a) Autoclave and current/potential measuring assembly. (b) Details of the anode assembly used in the current/potential measurements. (c) Details of the anode assembly used in the measurement of pH of the crevice solution.
2. Time dependence of current and potential for Grade-12 titanium crevice in diluted (by a factor of ten) Brine A. The closed and open circles represent uncoupled potentials of the freely exposed cathode disk and the anode assembly, respectively. The steady state test temperature is $\sim 150^{\circ}\text{C}$.
3. Time dependence of current and potential for a Grade-12 titanium crevice in acidic Brine A ($\text{pH} = 4.2$). The closed and open circles represent the uncoupled potentials of the cathode and anode. The steady state test temperature is $\sim 150^{\circ}\text{C}$.
4. Time dependence of current and potential for a Grade-2 titanium crevice in Brine A.
5. Severely corroded Grade-2 titanium crevice anode after the test described in Figure 4.
6. Freely exposed Grade-2 titanium crevice cathode after the test described in Figure 4. Note the unusual loss of metal in the upper corner.
7. A Grade-12 titanium crevice anode after the test in dilute Brine A showing corroded areas around the circumference. The central area shows only minor oxide film formation.

8. The pH measuring anode used in the same test as in Figure 7. Note decreased corrosion near the wells.
9. An SEM micrograph of early stages of pit formation in a Grade-12 titanium crevice where the crevice product has not filled the pit.
10. An optical micrograph of the pits on a Grade-12 titanium crevice specimen. Note the outgrowth of oxide as corrosion continues beneath the pit.
11. An optical micrograph of the surface of a Grade-12 titanium crevice specimen showing the alignment of oxide.
12. A vertical cross-section through a pit formed on a Grade-12 titanium anode specimen.

(a)

(b)

(c)

Figure 1. Design of the testing equipment for crevice corrosion under hydro-thermal conditions (diagram not to scale). (a) Autoclave and current/potential measuring assembly. (b) Details of the anode assembly used in the current/potential measurements. (c) Details of the anode assembly used in the measurement of pH of the crevice solution.

Figure 2. Time dependence of current and potential for Grade-12 titanium crevice in diluted (by a factor of ten) Brine A. The closed and open circles represent uncoupled potentials of the freely exposed cathode disk and the anode assembly, respectively. The steady state test temperature is $\sim 150^{\circ}C$.

Figure 3. Time dependence of current and potential for a Grade-12 titanium crevice in acidic Brine A (pH = 4.2). The closed and open circles represent the uncoupled potentials of the cathode and anode. The steady state test temperature is $\sim 150^{\circ}\text{C}$.

Figure 4. Time dependence of current and potential for a Grade-2 titanium crevice in Brine A.

Figure 5. Severely corroded Grade-2 titanium crevice anode after the test described in Figure 4.

Figure 6. Freely exposed Grade-2 titanium crevice cathode after the test described in Figure 4. Note the unusual loss of metal in the upper corner.

Figure 7. A Grade-12 titanium crevice anode after the test in dilute Brine A showing corroded areas around the circumference. The central area shows only minor oxide film formation.

Figure 8. The pH measuring anode used in the same test as in Figure 7. Note decreased corrosion near the wells.

Figure 9. An SEM micrograph of early stages of pit formation in a Grade-12 titanium crevice where the crevice product has not filled the pit.

Figure 10. An optical micrograph of the pits on a Grade-12 titanium crevice specimen. Note the outgrowth of oxide as corrosion continues beneath the pit.

Figure 11. An optical micrograph of the surface of a Grade-12 titanium crevice specimen showing the alignment of oxide.

Figure 12. A vertical cross-section through a pit formed on a Grade-12 titanium anode specimen.