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ABSTRACT

I. ALUMINUM

Studies on electrochemical aspects of the corrosion of aluminum alloys 5454 and 6061 were conducted in 1 M NaCl at 150°C in a titanium dynamic loop facility. Corrosion rates were followed with time by measurement of the polarization resistance of the specimens. The results show that the 5454 alloy is superior to the generally recommended 6061 alloy in corrosion resistance under all conditions studied. Polarization curves of the alloys were measured under a variety of conditions in order to determine the nature of the difference in corrosion properties. The results are generally similar to those obtained by other workers at lower temperatures, except for certain complications which appear mainly at the higher temperature of this study.

A pronounced minimum exists in the corrosion rate of aluminum and its alloys in chloride solutions in the vicinity of neutrality. Changes in the polarization curves of anodic and cathodic processes occurring at the aluminum-electrolyte interface with pH provide a kinetic basis for understanding this and other aspects of the corrosion behavior. At low potentials the rate of the anodic or corrosion reaction is independent of the electrode potential, but increases with increasing pH. The rate of the anodic process is controlled by the rate of mass transport of hydroxide ions to the oxide-solution interface. At higher potentials in the presence of chloride ions, the anodic

polarization curve exhibits a pitting potential which is independent of the anodic current density. The pitting potential does not vary with pH but decreases with increasing chloride concentration. The cathodic reaction in alkaline solution consists of the discharge of water molecules to form molecular hydrogen; this process is pH-independent. With increasing acidity, discharge of hydrogen ions becomes increasingly important. The minimum corrosion rate represents a compromise between the decrease in the rate of the transport-controlled anodic reaction and the increase in the rate of the cathodic hydrogen-evolution reaction with increasing acidity.

The transport-controlled rate of the anodic process depends on solution velocity and on the rate of the cathodic process, both of which affect the local pH at the oxide-solution interface. The rate of the anodic reaction also decreases with time at constant pH and solution velocity and is affected by the rate of refreshment of the solution in the loop and by the ratio of area of corroding specimens to solution volume. These effects can probably be understood on the basis of growth and dissolution kinetics of a porous outer layer which is known to exist on aluminum in high-temperature aqueous solutions. Other complications to the interpretation of polarization curves include Ohmic effects which occur in the measurements at high current densities and effects of dissolved oxygen in solution.

Comparison of polarization curves of the 5454 and 6061 alloys shows that the rate of the cathodic hydrogen-evolution reaction on the 6061 alloy is considerably greater than that of the 5454 alloy. The enhanced rate of the cathodic process on the 6061 alloy accounts for its greater corrosion

rate at any pH and for its susceptibility to pitting attack. Catalysis of the cathodic process on the 6061 alloy may be attributable to its copper content.

II. TITANIUM

Drastic, though extremely erratic, corrosion of titanium has been observed in saline waters at temperatures of 100⁰ to 200⁰C. The corrosive attack was first encountered in the loop studies of aluminum corrosion described above. It has been observed in loop and autoclave experiments with one and two molar sodium chloride solutions and synthetic sea water. Specimens exposed to treated sea water in the water box of the number one effect of the Freeport Desalination Plant also showed the attack. Crevices favor initiation of the attack with contact areas between plastics and titanium tending to promote the frequency of attack better than metal to metal contact. Once initiated, however, the corrosion process is often self-sustaining and continues beyond the confines of the crevice. Further, in a number of instances the attack apparently initiated at micro crevices or surface imperfections such as laps, fissures, or inclusions. The frequency and severity of attack vary directly with temperature and inversely with pH; the attack was not observed at pH values higher than 8.7. While very capricious in terms of initiation, rate, and extent of attack, penetration rates in excess of several hundred mils per year have often been observed. Of nine commercially available titanium alloys which have been tested, only the Ti-0.15% Pd alloy has shown demonstrable increased resistance to the

attack. It apparently is not immune, however, since pustules were initiated under Teflon insulation washers after 82 days exposure in the Freeport Plant.

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I. ALUMINUM

Aluminum can be employed as a resistant material of construction in contact with chloride solutions provided certain precautions are observed, particularly with respect to solution composition, pH, and galvanic couples with other metals.¹ Among commercially available aluminum alloys, important differences exist in corrosion behavior which suggested the need for comparative studies of the corrosion of aluminum alloys under dynamic conditions. Titanium loop studies in NaCl solutions have shown the 5454 alloy (0.8% Mn, 2.7% Mg, 0.1% Cr) to be the most resistant to corrosion of eleven commercially available alloys tested (EC, 1100, 3003, 3004, 4032, 5050, 5052, 5154, 5454, 6061, X8001).² Thus in short term comparative tests (~200 hr, pH 6.5, 150°C, 1 M NaCl) the generally recommended 6061 alloy (0.8% Si, 0.25% Cu, 1.0% Mg, 0.25% Cr) corroded three to eight times as fast as the 5454 alloy. The 5454 alloy also exhibited less pitting attack. In order to investigate more precisely the nature of differences in corrosion behavior of aluminum alloys, measurements of polarization curves and other electrochemical aspects of aluminum corrosion were conducted in a small titanium loop. Some results of these measurements are presented below.

High-Temperature Titanium Loop for Electrochemical Studies of Corrosion

Figure 1 shows schematically the corrosion loop facility which was developed for the measurement of electrochemical behavior of aluminum and

other alloys in high-temperature salt solutions. The loop, constructed entirely of titanium, is equipped with a heater and a pump capable of circulating the 650 ml volume of solution past the electrode surfaces at linear velocities ranging, usually, from 8 to 24 ft/sec, depending on electrode diameter. Provisions are available for continuous addition and withdrawal of fresh solution, if desired. Other features include a sampling valve, a metering pump for injection of acid or base for control of pH, and provisions for deaerating, aerating, or oxygenating solutions to be circulated in the loop.

Details of the electrode holder assembly are shown in Fig. 2. Electrodes are machined in the form of hollow cylinders from commercial stock. Each electrode is isolated from the loop and from other electrodes by use of silicone rubber gasket insulators. Electrolyte circulates past the interior surfaces of the electrodes, which were used in the "as-machined" state. The polarizing electrode, constructed of titanium, occupies a central position in the electrode holder; titanium rods welded to this central electrode extend axially through the electrolyte inside the other two electrodes. This arrangement minimizes IR drops in solution between the test specimens and the polarizing electrode and promotes uniformity of current density distribution.

Electrode potentials were measured on a high-impedance electrometer-recorder combination with respect to externally situated (room temperature) saturated calomel electrodes which were bridged into the loop solution by use of an asbestos wick assembly similar to that described by Bacarella and

Sutton.³ Aluminum electrodes (Fig. 2, specimen Nos. 1 and 3) were polarized galvanostatically by use of a conventional current source constructed from high-voltage batteries (135 v) of large capacity and high resistances. Interior surfaces of the electrodes were employed in the "as-machined" state.

Corrosion Rate Measurements. Corrosion rates of aluminum alloys 5454 and 6061 were followed as a function of time in 1 M NaCl at 150°C by use of polarization resistance measurements.⁴⁻⁶ The limiting slope of the polarization curve of a metal at small values of applied current (polarization resistance) is inversely proportional to the corrosion rate. In general, corrosion rates decrease with time until steady-state rates are attained in periods of time which depend on experimental variables such as pH, solution flow rate, rate of refreshment of solution, and others. Similar observations on changes of corrosion potential and corrosion rate with time have been reported.⁷⁻¹¹ The rate measurements show that the 5454 alloy is the more resistant to attack under these conditions, in agreement with observations on comparative weight loss over both short and extended periods of time.² In order to increase our understanding of the observed differences in corrosion behavior of these alloys, other experiments were conducted on the electrochemistry of reactions occurring at the aluminum-electrolyte interface.

Variation of Corrosion Potential and Corrosion Rate with pH. Figure 3 shows how the corrosion potential (measured vs. the saturated calomel electrode) of the 5454 alloy varies with pH. The current densities of anodic and cathodic interfacial reactions are equal at the corrosion of open-circuit potential. In weakly acidic solutions the corrosion potential is independent

of pH, while in alkaline solutions the potential decreases with increasing pH. This behavior is consistent with results of other investigators obtained in chloride solutions at lower temperatures.^{7,12,15} Experimental points shown in Fig. 3 represent the average (± 5 mv) of three determinations at each pH value.

A pronounced minimum exists in the corrosion rate -pH relation of aluminum and its alloys in chloride solutions in the vicinity of neutrality.^{7,12,13,16-18} Our results are quite similar to those reported by Troutner,¹⁷ at a lower temperature, except that corrosion rates in 1 M NaCl at 150°C are influenced more by the solution velocity and by the accumulation of corrosion products in the system. Increased solution velocity increases corrosion rate somewhat, particularly in alkaline solutions. The beneficial effect of corrosion products in solution noted under these conditions is in agreement with observations of others.^{11,9} Reasons for the existence of a minimum in the corrosion rate of aluminum and for the observed variation of corrosion potential with pH may be understood on a kinetic basis by reference to the polarization curves²⁰⁻²¹ of the anodic and cathodic reactions which occur at the aluminum-electrolyte interface.

Kinetic Interpretation of the Effect of pH on Aluminum Corrosion. Figure 4 shows schematic polarization curves which were constructed on the basis of experimental data accumulated on the 5454 alloy in 1 M NaCl at 150°C. Parameters shown in Fig. 4 are characteristic of the potentials and current densities observed in the real system, except that certain factors (discussed below) which produce variations in behavior are omitted. Curves ABC, A'B'C,

and A"B"C represent anodic polarization curves for the aluminum dissolution reaction as a function of pH. At low potentials (cf. AB, A'B', and A"B") the rate of the corrosion reaction is independent of the electrode potential, but increases with increasing pH. Corrosion is uniform over the metallic surface in this region. As shown by Kaesche,^{14,22} the corrosion rate in this region is controlled by the rate of mass transport of hydroxide ions to the oxide-solution interface. The interfacial reaction is so fast that the mass transport process determines the over-all rate. Further verification of this fact is provided by the work of Kolthoff and Sambucetti²³ who found that hydroxide ions yield well-defined anodic diffusion currents on the aluminum electrode.

In the presence of chloride ions, the anodic polarization curve of aluminum exhibits a critical potential which cannot be exceeded (in the steady state). At this potential, the pitting potential (BB'B"C in Fig. 4), pits form on the electrode surface and exist simultaneously with passive areas. The potential exhibited by the pitting surface in the steady state is essentially independent of the anodic current density. The nature of the pitting process and the properties of the pitting potential have been the object of numerous studies.^{8,10,14,22,24-37} The pitting potential of aluminum is independent of pH but becomes less noble with increasing chloride concentration.

The cathodic reaction in alkaline solutions is independent of pH (cf. DG in Fig. 4); this process consists of the reduction of water molecules to form molecular hydrogen. With increasing acidity, discharge of hydrogen ions becomes increasingly important (D'EF and D"E'F' in Fig. 4); lines D'E and D"E'

correspond to activated discharge of hydrogen ions and segments EF and E'F' correspond to diffusion-limited rates of this reaction. The reason for the existence of a minimum in the corrosion rate -pH relation of aluminum in chloride solutions is evident from the curves in Fig. 4. In alkaline solution the corrosion potential and corrosion current are determined by the intersection of the anodic curve A"B" and the cathodic curve DG [point (1) in Fig. 4]. With increasing hydroxide ion concentration, the transport-controlled rate of the anodic or corrosion reaction increases and therefore the intersection of the anodic polarization curve with the cathodic polarization curve (DG) shifts to lower potentials and higher current densities. This accounts for the decrease of corrosion potential with pH in alkaline solutions observed in Fig. 3. In acidic solution the cathodic polarization curve (D"E'F'G) intersects the anodic curve (ABC) at the pitting potential [point (3) in Fig. 4]. With increasing acidity, the corrosion potential remains at the pitting potential (cf. Fig. 3) while the corrosion current increases as a consequence of the increased rate of reduction of hydrogen ions; the severity of the pitting attack increases accordingly. The minimum in the corrosion rate -pH relation represents a compromise between the decrease in the rate of the transport-controlled anodic reaction and the increase in rate of the cathodic hydrogen-evolution reaction with increasing acidity [cf. point (2) in Fig. 4]. The minimum rate occurs when the rate of the transport-controlled anodic reaction becomes small enough with increasing acidity so that the intersection of anodic and cathodic polarization curves occurs at the pitting potential. For this reason the break in

the corrosion potential - pH relation (cf. Fig. 3) coincides with the minimum in the corrosion rate -pH relation. One can conclude that the limit of corrosion resistance of aluminum and its alloys in chloride solutions is determined by the position of the pitting potential, which varies with chloride ion concentration, in relation to the polarization curve of the cathodic process.

Effect of Solution Velocity. The ideas expressed schematically in Fig. 4 are in general agreement with the findings of Kaesche.^{14,22,33} However, certain effects occur at the higher temperature of our study (150°C) which should be considered in the interpretation of the experimental polarization curves. We find that the magnitude of the current corresponding to the transport-controlled anodic reaction (e.g., A"B" in Fig. 4) depends on the solution velocity. This effect is shown in Fig. 5, where curves A and B are the polarization characteristics of type 5454 alloy measured in 1 M NaCl at 150°C, pH 9.0. In alkaline solutions, where transport of hydroxide ions to the oxide-solution interface controls the rate of the uniform dissolution reaction, an increase of solution velocity probably causes a decrease in the diffusion layer thickness at the interface. This permits a higher flux of hydroxide ions to the electrode surface and thus a greater over-all corrosion rate. On the other hand, velocity effects appear to be negligible in acid solutions (cf. curve C in Fig. 5) where the electrode undergoes pitting attack at the pitting potential, unless the rate of the cathodic process is also influenced by mass transfer of hydrogen ions.

Effect of Cathodic Polarization on Corrosion. The schematic anodic polarization curves of Fig. 4 should be modified to reflect the phenomenon of

"cathodic corrosion" of aluminum, as studied by Kaesche.¹⁴ When aluminum is polarized with cathodic current, the reduction of hydrogen ions or water molecules to form molecular hydrogen causes an increase of the local pH at the interface. This increase in local pH enhances the dissolution rate of the superficial oxide layer. One can also conclude that if impurities of low hydrogen overvoltage are present or if aluminum is connected to a less noble metal, the corrosion rate will be increased.

Effects of the Structure of the Oxide Layer and of Time. Our measurements in alkaline solutions (cf. curves A and B of Fig. 5) show that the rate of the anodic reaction decreases with time at constant pH and solution velocity; this is particularly noticeable during the first few hours of an experiment. Since the rate of the cathodic reaction is essentially independent of time, we observe a corresponding ennobling of the corrosion potential and a decrease in the corrosion rate. Other variables associated with this effect appear to be the rate of refreshment of the solution in the loop and the ratio of area of corroding specimens to solution volume. Evidence is available for the existence of a duplex film on aluminum corroding in high-temperature aqueous solutions and for the beneficial effects of dissolved corrosion products on the corrosion rate.^{11,17,19,38,39} Perhaps the decrease with time of the rate of the anodic reaction in our experiments can be accounted for by the kinetics of growth and dissolution of the so-called "outer" film, which is believed to possess considerable porosity. In this case, an increase in the thickness of the outer layer could very effectively increase the diffusion path for the transport of hydroxide ions to the surface of the

"inner" compact oxide layer. All other kinetic interpretations of polarization curves would then remain the same as discussed above, except for the influence of the outer film thickness on concentrations of reactant ions. If this interpretation is correct, effects of solution refreshment rate, of specimen area to solution volume ratio, and of corrosion products in solution are probably associated with the kinetics of growth and dissolution of the outer porous oxide layer; this in turn affects the dissolution kinetics of the inner layer by altering the flux of reactants (OH^- , in particular) due to diffusion, migration, and convection.

Ohmic Effects. Still another factor which affects interpretation of polarization curves can be seen in Fig. 5. The polarization curve of the cathodic process (hydrogen evolution from solvent molecules) exhibits considerable curvature at the higher current densities when plotted semi-logarithmically. We find that conventional, linear polarization curves²⁰ may be obtained in most cases by a correction procedure involving subtraction of an Ohmic contribution to the electrode potential. Some measurements suggest that the resistance contribution increases with time. Conceivably, restricted access of solution to the surface of the inner layer imposed by the porous outer layer could be responsible for the Ohmic resistance which is included in the measurement of cathodic polarization curves. This interpretation is also consistent with an increase of the Ohmic contribution with time due to growth of the outer oxide layer. Alternatively, the inner layer may itself possess sufficient electronic resistance to produce significant IR drops in the measured cathodic polarization curves. Ionic and electronic conductivities and distributions of defect concentrations in aluminum oxide layers have been studied by a number of workers.⁴⁰⁻⁴⁵

Effect of Dissolved Oxygen. In neutral chloride solutions, molecular oxygen dissolved in solution can be reduced at the oxide-solution interface; in some cases the reaction rate may even be larger than that of the hydrogen-evolution reaction so that the corrosion rate is essentially controlled by the oxygen-reduction reaction.^{8,24} The effect of oxygen reduction on the corrosion of the 5454 alloy in 1 M NaCl, pH 8.1, at 150°C is shown in Fig. 6. In deaerated solution at this pH, the cathodic process consists of the reduction of solvent molecules to form molecular hydrogen and the aluminum corrodes uniformly at a very low rate; the corrosion potential lies below the pitting potential. Admission of oxygen to the system increases the total cathodic current; at the potentials in Fig. 6 the reduction reaction of O₂ is essentially under mass transfer control. In oxygenated solution, the reduction current is so large that the corrosion potential of the aluminum is pulled up to the pitting potential and severe, non-uniform, pitting attack occurs. For this reason, oxygenated solutions and traces of noble metals which can catalyze reduction reactions should be avoided whenever possible.

Comparison of 5454 and 6061 Alloys. A comparison of polarization curves of the 5454 and 6061 alloys in 1 M NaCl, pH 8.1, at 150°C is shown in Fig. 7. Corrosion rates are rather high in this case; the loop solution was replenished with fresh stock solution at a rate of about one loop volume per hour, so that the full beneficial effect of accumulated corrosion products on the corrosion rate was not achieved. Figure 7 shows that the rate of the hydrogen-evolution reaction on the 6061 alloy is considerably greater than that of the 5454 alloy.

Other measurements show this to be true at any pH. The curvature of the cathodic polarization curves is due to the Ohmic effect discussed above. Under the conditions of Fig. 7, the 5454 alloy undergoes uniform dissolution below the pitting potential, while the high rate of the cathodic process maintains the 6061 alloy at the pitting potential. The enhanced rate of the cathodic process on the 6061 alloy, compared to the 5454 alloy, therefore accounts for its greater corrosion rate at any pH and for its susceptibility to pitting attack. We are inclined to attribute catalysis of the cathodic process on the 6061 alloy to the copper content (0.25%). Copper has the lowest hydrogen overvoltage of any of the major alloying elements in either the 5454 or 6061 alloys. Similar catalytic effects of trace elements have been studied by others.^{46,47}

The differences in corrosion behavior of the 5454 and 6061 alloys which were detected in earlier loop experiments are shown by the polarization measurements to be a consequence of the enhanced rate of the cathodic reaction on the 6061 alloy compared to the more resistant 5454 alloy. Our results show that measurement of polarization curves of metals and alloys in high-temperature loops is a promising technique for rapid assessment and comparison of corrosion resistance. In addition, information is obtained on the nature of rate-controlling steps of corrosion reactions which is difficult to obtain by any other method of corrosion research.

II. TITANIUM

Titanium is reported to be immune to all forms of corrosive attack in ambient sea water.⁴⁸⁻⁵¹ Various investigators⁵⁰⁻⁵² have also shown it to

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 - (49) F. R. LaQue and H. L. Copson, Corrosion Resistance of Metals and Alloys, 2nd ed., pp. 654-656, Reinhold, New York, 1963.
 - (50) L. B. Golden, I. R. Lane, and W. L. Acherman, Ind. and Eng. Chem. 44: 1930-1939 (August 1952).
 - (51) D. Schlain, "Corrosion Properties of Titanium and Its Alloys," Bureau of Mines Bulletin No. 619, 1964.
 - (52) P. J. Gegner and W. L. Wilson, Corrosion, 15: 341t-350t (July 1959).
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be resistant to attack in most chloride solutions at elevated temperatures. For example, it was reported inert or nearly so in concentrated ferric, nickel, mercuric, cupric, manganous, ammonium, and magnesium chloride solution at temperatures of 100° to 155°C. However, under similar conditions in other chloride solutions, such as those of zinc, calcium, or aluminum, erratic behavior has been encountered. Gegner and Wilson⁵² observed corrosion rates ranging from nil to >60 mpy on duplicate specimens exposed to 62% calcium chloride at 154°C. Other investigators⁵¹ have also noted gross variations in the corrosion resistance of titanium to concentrated chloride solutions with relatively modest changes in temperature and/or concentration.

Observations of titanium corrosion made in connection with the aluminum studies discussed above, and in resultant other studies, suggest such erratic corrosion of titanium in chloride solutions may be a more general, and serious problem than has been appreciated thus far.

HIGH TEMPERATURE LOOP OBSERVATIONS

The corrosive attack was initially observed on titanium clamping bands used in the assembly of loop specimen holders. Open and assembled holders are shown in Fig. 8; note the three bands holding the halves of the holder together and the Teflon sleeves used to insulate the pin specimens from the titanium holder. Strips of Teflon are also often used to cover the ends of the pins to eliminate the possibility of inadvertent contact between the bands and pins, so both metal to metal and metal to Teflon crevices are formed under the bands. The assembled specimen holders are fitted into $1\frac{1}{2}$ -in. titanium pipe sections flanged into titanium loops and equipped with fittings which direct the loop fluid flow through the channel in the holder (see Fig. 9). Thus the bands are exposed to the test solution in a semistagnant annulus ($\sim 1/32$ in. thick) between the holder and the pipe wall.

Figure 10 shows a number of clamping bands (made from 0.008-in. A55 titanium sheet) after exposure to pH 6.5 two molar sodium chloride at 150°C for 192 hr. Seven of the twenty bands show gross attack, but the remaining thirteen show none (the small holes in and near the welds were produced in fabrication). Similar attack has been observed under the Teflon sleeve insulation on pin specimens, but in all the experiments conducted thus far the initiation, rate, and extent of the attack has been very erratic. This inconsistency has made quantitative evaluation of the effects of various parameters very difficult; however, some trends have been indicated by the accumulated observations.

Presence of a Crevice. Crevices seem to promote initiation of the attack and contact areas with Teflon are more effective than metal to metal contact. A strong correlation between the areas of attack and contact with Teflon in the early observations suggested that the attack might result from breakdown of the protective oxide film by small amounts of fluoride released by the Teflon. Autoclave tests with bolted coupon crevice specimens in the absence of Teflon, however, eliminated this hypothesis; although, the possibility that it plays a part in the promotion of the attack in Teflon contact areas still exists. It is our belief that the tight crevice formed in contact with Teflon is the important factor. We have also observed the attack in areas of contact with silicone rubber gaskets, see Fig. 2; and others⁵³ have noted similar cre-

(53) L. W. Gleekman, Chem. Eng. 70: 224 (November 11, 1963).

vice attack in areas of contact with rubber and Teflon in wet chloride service.

While macro crevices promote the attack, it is also clear that they are not required for its initiation or continuation. Note in Fig. 3 that the fifth band from the top in the middle column was severed but apparently kept on corroding, as did the other bands showing attack, after the crevice was eliminated by perforation of the band. This has also been observed in autoclave tests in which the corrosion continued well beyond the confines of the crevice. In addition, a number of instances have been observed where the attack was initiated in the absence of a macro crevice. Examinations of specimens on which the attack was incipient indicates laps, inclusions, etc., formed during the metal fabrication, provide micro crevices at which the attack may be initiated.

Temperature. The effect of temperature on the frequency of attack is shown in Table 1. The data given are for pins and bands exposed in loop runs. The attack has been observed only once at 100°C, on a pin specimen under the Teflon sleeve after 1178 hr exposure; but the frequency of attack increases with temperature. Note, however, the extremely erratic results shown by the wide range in the percent attacked in a given run. At 150°C the attack on the bands usually rapidly penetrates the 8 mil metal thickness and then spreads by consuming the entire thickness of the band along a relatively sharply defined front. At 200°C the attack is often more general, spreading over the surface on which it initiates more rapidly than it consumes the band thickness.

pH. The effect of pH is shown by the data in Table 2. The attack has been observed at pH values as high as 8.7, and the frequency appears to be inversely dependent on pH. Again, however, the initiation of attack is very erratic as is the rate after initiation. Similar erratic results have been obtained in autoclave experiments at 150°C. No data at lower pH values were obtained from loop runs for fear of excessive damage to the equipment.

Time. In most cases, those specimens which are attacked begin to corrode very shortly after reaching temperature. Initiation of attack on the bands has been observed after twenty-four hours exposure at pH 6.4 (2 M NaCl) at 150°C. Perforated bands have been observed after 188 hr at 150°C (1 M NaCl, pH 6.5) and after only 44 hr at 200°C (1 M NaCl, pH 6.0). Since the bands were 8 mils thick, this corresponds to penetration rates of 1.6 in. per year and 0.4, respectively. The rate of attack varies substantially, however, and often the corrosion stops completely. Thus, of fourteen pins

Table 1. Effect of Temperature on Titanium Corrosion

Conditions: 1 or 2 M NaCl, pH 5.5-6.5

°C	Pins				Bands			
	No. of Runs	Total No. Exposed	Percent Attacked* Average	Per Run	No. of Runs	Total No. Exposed	Percent Attacked* Average	Per Run
100	3	24	4	0-16	6	102	0	0
150	2	17	82	0-100	18	346	32	0-83
200	4	106	79	56-94	3	98	64	48-83

* Includes all observable instances of initiation of attack.

Table 2. Effect of pH on Titanium Corrosion

pH Range	Pins				Bands			
	No. of Runs	Total No. Exposed	Percent Attacked Average	Range	No. of Runs	Total No. Exposed	Percent Attacked Average	Range
4-5	1	8	100	—	—	—	—	—
5-6	1	3	0	—	2	34	32	18-47
6-7	2	22	91	86-100	10	192	34	0-83
7-8	1	2	50	—	6	126	10	0-32
8-9	3	6	17	0-100	3	62	5	0-14
8-10.3	2	6	0	0	2	40	0*	

* These runs were made before we were aware of the problem, so the bands were not examined carefully as in the later runs, but no gross attack was noted.

exposed in a succession of loop runs (2 M NaCl, pH 6.5), all showed some attack after 98 hr at 150°C. Twenty-one of the twenty-eight areas of contact with Teflon showed observable corrosion. The attack varied from a few pustules to generalized penetration to a depth of eight or ten mils.

Exposure for an additional 219 hr produced attack in two additional Teflon contact areas and continued corrosion in only six of the twenty-one areas which showed attack after the first exposure. Two hundred and sixty-one hr of further exposure resulted in no visually observable additional attack. Similar results have been obtained in other loop run series.

The rapid initiation and the later termination of the attack were also confirmed in an experiment carried out in a quartz tube so that the process could be viewed. The specimen was a strip of the 8 mil stock from which the bands are made, and a crevice was formed by bending a corner of the strip tightly over a piece of Teflon. Bubbles of gas were observed at the edges of the crevice 105 minutes after the tube was brought to 150°C; the gas was later shown to be hydrogen. Sixty-six hours later the reaction, as indicated by gas evolution, had stopped.

Alloys. A variety of titanium alloy pins has been exposed to sodium chloride and synthetic sea water solutions in several loop runs. The alloy compositions are given in Table 3 and the results are summarized in Table 4. Eight of the nine alloys tested showed the usual erratic attack in areas of contact with the Teflon insulating sleeves. Only the Ti-0.15% Pd alloy consistently resisted attack in these exposures, even at 200°C. None of thirty palladium alloy pins exposed showed microscopically observable attack, compared to 68% of the specimens of the other alloy compositions.

Table 3. Titanium Alloy Compositions Tested

Alloy	Nominal % Composition								
	<u>Al</u>	<u>Cr</u>	<u>Mn</u>	<u>V</u>	<u>Zr</u>	<u>Nb</u>	<u>Ta</u>	<u>Fe</u>	<u>Pd</u>
A45	(Commercial Purity - >99.2% Ti)								
A55	(Commercial Purity - >99.0% Ti)								
Cast Ti	(Unalloyed)								
Al-Cr	3.5	4.9						0.2	
Al-Mn	4.2		4.6					0.3	
Al-V	6.4			4.2				0.2	
821	7.4					2.0	1.1	0.2	
881	8.2				8.5	0.7	0.5		
Ti-Pd									0.15

Table 4. Corrosion of Titanium Alloys in Saline Waters

Conditions: Synthetic Sea Water and NaCl Solutions
 ~0.5-2 M, pH 6-7, pins with Teflon Sleeves

	150°C		200°C	
	<u>Pins Exposed</u>	<u>Pins Attacked</u>	<u>Pins Exposed</u>	<u>Pins Attacked</u>
A45	14	3	12	9
A55	11	6	12	10
Cast	6	0*	—	—
Al-Cr	2	2	—	—
Al-Mn	5	3	12	12
Al-V	5	3	9	7
821	4	4	9	8
881	5	2	9	9
Ti-Pd	22	0	8	0

* Four coupons were also exposed and all four were attacked in Teflon contact areas.

Pretreatments such as annealing, anodizing, pickling, and air oxidation did not alter pin specimen or band behavior significantly. Resistance to attack seemed improved, but in all cases some specimens were attacked and the lower frequencies may have been fortuitous.

Loop Components. In spite of the severity of the attack on the bands and pins, little difficulty has been experienced with the titanium loops and equipment in thousands of hours of operation. Several factors may account for this:

1. Prior to use in these studies, the loops were used with strongly oxidizing solutions to temperatures as high as 300°C. Consequently, the surfaces are generally coated with heavy oxide films which may reduce the likelihood of attack.

2. Crevices were minimized by design and welded construction.

3. Most surfaces are exposed to rapidly flowing solution.

However, some problems have been encountered. The first of these was observed in the areas of contact with the silicone rubber gaskets in the test assembly for electrochemical studies (see Fig. 2). The attack initiated in the crevices between the large titanium end flanges and the silicone rubber gaskets and then invaded the conical flange apertures. After ~5000 hr of operation on one molar sodium chloride solution largely at 150°C, the flanges have been damaged sufficiently to require replacement.

Penetration of one of the one and a half inch schedule 90 titanium pipe sections into which the corrosion specimen holders are inserted has also been encountered. This occurred at the point labeled C in Fig. 9, and the large

shallow pit which resulted in the failure is shown in Fig. 11; the penetration occurred a little below the center of the pit. Penetration of the 0.2-in. pipe wall occurred after a total of 8468 hr of operation principally with one and two molar sodium chloride solutions at pH's in the range 5.5 to 7.2. The temperature history was 2808 hr at 100°C, 5374 hr at 150°C, and 286 hr at 200°C. A careful examination of the loop as a result of the above failure revealed additional smaller areas of attack at the locations indicated by C' in Fig. 9; these are areas exposed only to flowing solution with no macro crevices of any kind.

Concentration. Loop runs were carried out with both one and two molar NaCl. No consistent differences in the attack on pins and bands were observed, so the data were combined in this report.

Aeration. The loop experiments have been run in two ways as regards aeration. In one case, the circulating solution was continuously refreshed with aerated solution which was pumped into the loop at a rate of one liter per hour (loop volume = 17 liters); in the other, the charge solution was "deaerated" by over-night evacuation, charged to the evacuated loop, and run with helium or nitrogen overpressure. Analyses of the gas from solution samples taken during such runs usually showed no oxygen but probably had a lower limit of detection of a few tenths of a ppm. The results obtained under the two conditions did not differ significantly.

Metallography. Metallographic sections through corroded areas of bands are shown in Figs. 12 and 13. Figure 12 shows the attack characterized by relatively rapid penetration of the band. Figure 13 shows the surface

spreading type attack, note that attack initiated on both surfaces of this band. The surface attack occurred on the side of the band exposed to the semistagnant solution annulus between the specimen holder and titanium pipe in which it was contained. The pustules shown on the other side of the band, usually characteristic of the penetration type attack, formed in the crevice between the band and the holder. Figure 13a shows the specimen as etched to bring out hydride formation; the black band between the bright metal and the gray oxide was identified as hydride by this procedure. The identification was confirmed by subjecting the specimen to a vacuum anneal at 800°C which decomposed the hydride and removed the hydrogen as shown in Fig. 13b. The presence of hydrogen in corroded areas has also been confirmed by vacuum fusion analyses. The light gray band at the edge of the corrosion front in Fig. 12 has also been identified as hydride.

SEA WATER

Loop experiments with synthetic sea water~~s~~ gave results consistent with those obtained with the sodium chloride solutions. Thus it appeared likely that the attack would also be encountered in actual sea water exposure, but experimental confirmation was desirable. Through the cooperation of Mr. H. D. Singleton, Office of Saline Water Resident Engineer at the Freeport Desalination Plant, three racks of commercially pure titanium specimens were exposed in a representative desalination plant environment. These racks contained metal-metal and metal-Teflon crevices. Two types of metal-metal crevices were included: bolted coupons and one-half inch tubes rolled into a one inch thick titanium plate to simulate a tube sheet joint. Metal-Teflon

crevices were formed by inserting Teflon sheet between some of the coupons and under Teflon washers used to insulate specimens from the rack. One pair of Ti-0.15%Pd coupons was included on the A rack; the crevice between these plates was metal-metal, but metal-Teflon crevices were also formed under Teflon insulation washers.

The three racks were exposed in the water box of the number one effect at the Freeport Plant; the brine conditions and exposure history are given in Table 5. Rack A was removed for examination after 12 days exposure. Attack had initiated in several metal-Teflon crevices but not in the coupon metal-metal crevices. Incipient attack appeared to be present in a simulated tube joint which was cut open. The Ti-0.15% Pd coupons showed no evidence of attack at this time; however, slight attack was observed in the threads of the mounting bolt under the Teflon washers used to insulate these coupons from the rest of the assembly. The rack was reassembled and returned for additional exposure.

Rack C was removed after 32 days and on examination gave results essentially the same as those described for Rack A above.

Racks A and B were removed for examination after a total of 82 days exposure. Rack B was in the same condition after 82 days as Rack A had been after 12 days. Attack had initiated only in areas of contact with Teflon and perhaps in simulated tube joints. If anything, the attack had progressed less than in similar locations on Rack A. Examination of Rack A revealed it to be unchanged except in two respects. The attack which had initiated in the mounting bolt threads under the Teflon used to insulate the Ti-0.15% Pd

Table 5. Temperature Exposure History of Racks Exposed in Freeport Plant

Conditions: Exposed in water box of No. 1 effect to normal
concentration deaerated brine after acid treatment
and neutralization for scale control, pH 6.8-7.5.

Temperature, °C	Days Exposed		
	<u>Rack A</u>	<u>Rack B</u>	<u>Rack C</u>
138	12 ^{a,c}	12	12
135	20	20	20 ^b
129	50 ^c	50 ^c	—

^a Removed after 12 days, examined and replaced.

^b Removed after 32 days, examined and replaced.

^c Removed after 82 days, examined and replaced.

alloy coupons had progressed substantially. The threads ($\frac{1}{2}$ -in. National Course) were completely destroyed and pits had penetrated about one-sixteenth inch into the bolt body beneath the thread roots. Also, the Ti-0.15% Pd alloy coupons showed attack for the first time; a number of pustules had formed under the insulating washers.

Although appreciable only in areas of contact with Teflon, the attack observed in the Freeport Plant racks was entirely similar to that observed in the loop experiments and is regarded as verification of the serious crevice corrosion of titanium by saline waters at elevated temperatures. Exposure of the specimen racks in the Freeport Plant is continuing.

DISCUSSION

While crevice corrosion has been demonstrated not to be a problem with titanium in ambient sea water, the observations described in this report indicate it may be of considerable concern at temperatures above 100°C. Thus, very aggressive but erratic corrosion has been initiated in crevices exposed to saline waters at temperatures of 150° and 200°C. The particular nature of the crevice plays an important, undefined part in the initiation of the attack, contact areas between plastics and titanium tending to promote initiation of the attack better than metal to metal contact. It has also been observed, however, that the attack may initiate at "micro crevices" such as surface laps, fissures, or inclusions produced during metal fabrication. Once initiated the corrosion process may be self-sustaining and continue outside the confines of the crevice or it may cease after a period of time. The parameters governing the outcome have not been established.

The observations suggest an interesting explanation of the attack in the absence of macro crevices encountered in piping flow areas after thousands of hours exposure without difficulty. The attack has only been observed in areas subject to mechanical deformation during the routine assembly of the flanged joints accompanying insertion of corrosion specimen holders in the loops. It is postulated that such deformation causes cracks in the heavy oxide scale present on the piping with resultant formation of micro crevices in which the attack initiates.

Metallographic sections through corroded areas bear a striking resemblance to the blister type pitting attack observed in concentrated chloride solutions

by Golden et al.⁵⁰ They attributed this attack to impurities in the metal such as magnesium chloride inclusions often found in powder metallurgy produced titanium, and stated that arc melted titanium with "very low magnesium chloride content" did not show such pitting. The specimens used in these studies were from arc melted material shown by spectrographic analyses to contain less than ten ppm magnesium (limit of detection). Thus it appears the magnesium chloride inclusions only provided sites for initiation of a type of attack to which titanium is generally susceptible in high temperature aqueous chloride solutions.

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TEST ASSEMBLY FOR ELECTROCHEMICAL STUDIES
OF DYNAMIC CORROSION

Fig. 3 Corrosion Potential of 5454 Aluminum Alloy as a Function of pH in 1M NaCl at 150°C.

Fig. 4 Schematic Polarization Curves of Anodic and Cathodic Reactions on Aluminum in Chloride Solution.

Fig. 5 Effect of Solution Velocity on Polarization Curves of 5454 Aluminum Alloy in 1M NaCl at 150°C.

Fig. 6 Effect of Oxygen Concentration on Cathodic Polarization Curves of 5454 Aluminum Alloy in 1M NaCl, pH 8.1, at 150°C.

Fig. 7 Comparison of Polarization Curves of 5454 and 6061 Aluminum Alloys in 1M NaCl, pH 8.8, at 150°C.

Fig. 8. Titanium Specimen Holder.

Fig. 9. Schematic Diagram of Titanium 100 gpm Solution Test Loop.

CONDITIONS:

150°C

2M NaCl

pH ~6.4

192 HOURS

Fig. 10. Corroded Specimen Holder Clamping Bands.

*PENETRATION OCCURRED AT POINT INDICATED BY P.

Fig. 11. Pit Penetration of $1\frac{1}{2}$ -in. Titanium Pipe.

ETCHANT-50 % GLYCERINE, 25 % HNO_3 , 25 % HF
 Fig. 12. Titanium Clamping Band Corrosion.

(a) BEFORE VACUUM ANNEALING

(b) AFTER VACUUM ANNEALING AT 800 °C

ETCHANT-50 % GLYCERINE, 25 % HNO_3 , 25 % HF

Fig. 13. Titanium Clamping Band Corrosion.