THE ROLE OF MULTI-VALENT METAL IONS

IN SUPPRESSING CREVICE CORROSION OF TITANIUM

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Introduction

Titanium is normally immune to corrosion in chloride solutions. However, at elevated temperatures and chloride concentrations it is subject to crevice corrosion (1,2), which can, under some circumstances, render it unsuitable for use in these environments. This phenomenon is encountered in sea water near the boiling point and in concentrated brine solutions where titanium is finding extensive use.

Griess (3) has presented evidence that crevice corrosion of titanium occurs when depletion of oxygen in the crevice causes the corrosion potential to decrease thus establishing a macrocell. The oxidation of titanium in the crevice is balanced by the reduction of oxygen or hydrogen ions outside the crevice. Hydrolysis of the titanium ions causes the pH of the crevice solution to decrease. Brown, et al (4) have demonstrated that a pH as low as 1.7 or lower can develop in a crack or a narrow crevice in titanium immersed in 3.5% NaCl solution (pH 6.5).

It has been known for many years that the presence of metal cations in solution would often reduce the corrosion of titanium in these solutions. Tomashov, et al reported on the passivating effect of platinum, copper and iron ions in the corrosion of titanium in 15% HCl. This effect has been confirmed by other investigators (5, 6) for these ions as well as other metals such as nickel, palladium, antimony, etc. Feige and Murphy (7) suggested that the addition of soluble nickel compounds in the crevice in the form of a paint might serve to passivate the crevice and stop any corrosion.
The work reported in this paper was undertaken to examine the effect of various multivalent metal ions on the reactions occurring in the crevice.

Experimental Procedure

The effect of various metal ion additions on the corrosion potential of titanium was measured in the apparatus shown in Figure 1. This consisted of two one liter flasks connected with a capillary tube so that only very limited diffusion could occur between the two solutions. This is essentially what occurs in a crack or crevice where only limited diffusion between the solution in the crevice and the bulk of the solution can occur. Each flask was fitted with an electrode of Ti-50A and filled with a saturated solution of NaCl. The whole assembly was immersed in a constant temperature oil bath and maintained at 200 F. The open circuit potential of each electrode was measured versus a saturated calomel reference cell using a Keithley 610B electrometer. Potential readings were arrived at by making successive readings at five minute intervals until no change was noted. The current flowing between the two electrodes, when they were connected externally, was also measured. The composition of the solution in one flask (representing the bulk solution) was held constant during the tests while the other was varied to represent conditions that may exist in the solution in a crevice.

All solutions used were made with reagent grade chemicals and distilled water. The electrodes were prepared from mill annealed C.P. titanium (grade Ti-50A) and pickled in 35% HNO₃-5%HF solution immediately before use.

Polarization measurements were made using a Wenking 61RS Potentiostat and an electrochemical corrosion cell similar to the one employed by Verink and Pourbaix (8).

Results

The open circuit potentials of the two electrodes were found to be almost identical at the start (-.32 volts vs SCE). Figure 2 is a plot of potential vs ion concentration. The heavy black line represents the potential of the cell corresponding to the bulk solution. This was quite reproducible and varied only a little from one run to the next. This line of course would represent a plot of potential vs time rather than concentration since no changes were made in this solution except to saturate it with air and chlorine by bubbling these through the solution.

The first data points at the left indicate the open circuit potentials of the two electrodes after air was bubbled through the bulk solution cell and argon through the crevice cell. These data points indicate a potential difference of about .1 volt due to
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Fig. 1. Cell for potential measurements.

Fig. 2. Effect of metal ions on potential.
differential aeration. The second data points show the effect of chlorine addition to the bulk solution cell which increased the open circuit potential of this electrode to +.3 volts making a difference of .7 volts between the two electrodes. The third set of points shows the change in potential that occurred in the crevice cell when sufficient HCl was added to lower the pH to 1. The potential decreased to -.76 volts, which is a very active corrosion region for titanium. A difference of potential at this point of over one volt was noted so under these conditions severe crevice corrosion could be expected.

Each run was identical to this point and the potentials reproduced quite well. From this point on metal ions were added to the solution representing the crevice in increments of 2 mg/l. The Fe+3 and Mo+6 moved the open circuit potential very strongly in the positive or passive direction with the first addition, indicating that very small concentrations of these ions are required for passivation. Cu+2 and Ni+2 required larger additions before passivation occurred. Addition of the ions of Al, Sn, and Mn up to a concentration of 24 mg/l had little effect on the potential.

Figure 3 is a plot of current versus ion concentration and shows much the same thing. Mo and Fe reduced the current flow sharply while Cu and Ni trailed off more slowly. Mn, Sn, and Al showed no decrease of current with increasing ion concentration. The Mn gave wild fluctuations which tended to return to the former level so no net reduction of current was obtained.

Figure 4 shows a series of polarization curves for Ti-50A in saturated NaCl solution with chlorine and nickel added. The cathodic curve for the solution containing both chlorine and nickel shows two breaks in the curve. The first corresponds to the limiting diffusion current for chlorine reduction and the second for the reduction of nickel ions. The cathodic curve for the solution containing only Ni ions shows a break in roughly the same region for nickel while the break attributed to chlorine is absent. The effect of these elements on the rest potential is also clearly shown. Saturated NaCl solution at pH6 gave a rest potential of -.328 volts vs SCE. The addition of sufficient NiCl2 to make the solution .05M increased the rest potential to 0. Saturation with chlorine gas caused the rest potential to increase further to +.11 volts vs SCE.

Discussion

It is postulated that titanium is subject to crevice corrosion in a brine solution containing oxygen or chlorine because the oxygen or chlorine in the crevice is consumed faster than it diffuses into the crevice from the bulk solution. As a result the corrosion potential of the metal in the crevice becomes more negative than the potential of the metal exposed to the bulk
Fig. 3. Effect of metal ion concentration on corrosion current.

Fig. 4. Polarization curves for Ti-50A in saturated NaCl solutions at 200°F.
solution as was demonstrated by the previously described experiment. This sets up an electrolytic cell with the metal surfaces in the crevice acting as the anode and the adjacent metal outside the crevice acting as the cathode. Metal dissolves at the anode under the influence of the resulting current and hydrogen is generated at the cathodic sites.

The titanium chlorides formed by the anodic reaction are unstable at neutral pH values and tend to hydrolyze forming Ti(OH)$_x$ and HCl according to the reaction 

$$\text{TiCl}_x + 3\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_x + 3\text{HCl}$$

thus reducing the pH and further accentuating the potential difference between the metal in the crevice and the bulk solution.

Hydrogen uptake efficiency measurements (9) indicate that unalloyed titanium will not absorb hydrogen from brine solutions at neutral pH. However, as the pH is lowered hydrogen absorption commences at about pH3 causing the formation of surface hydride films.

The hydride films formed by the cathodic reaction are believed to be much less protective than the normal oxide film and should in turn become anodic sites with consequent dissolution of metal. It is suggested that this may account for the observation that corrosion, although commencing in a crevice, will frequently spread over considerable areas of the surface well removed from the crevice.

In the experimental work previously described it was found that the addition to the crevice solution of small amounts of multivalent ions of such metals as iron, molybdenum, copper and nickel tend to shift the corrosion potential of the titanium exposed to the solution back in the positive direction, thus counteracting the effect of oxygen or chlorine depletion and pH changes. It is believed that these ions are effective because they are more easily reduced than hydrogen ions and thus accelerate the cathodic reaction causing the potential to shift in the positive direction resulting in a corresponding increase in the anodic reaction to the point that it reaches the critical current density for passivation and the surface oxidizes and becomes passive.

A similar concept was advanced by Tomashov (4) to explain the passivating effect of multivalent metallic ions on titanium undergoing general corrosion. Speaking specifically of Pt$^{+4}$, Cu$^{+2}$ and Fe$^{+3}$, he states, "these ions act as effective cathodic depolarizers, inasmuch as the potential at which they discharge is considerably more positive than the hydrogen ion discharge potential. Aside from the fact that in separating galvanically with cathodic depolarization, Pt and Cu ions form new effective cathodic areas, enhancing still more the rate of the cathodic process." It seems likely that the same mechanism can be used to explain the passivating effect of these ions in a crevice.
Theoretical considerations lead to the idea that multivalent metal ions supplied only in the crevice might maintain this area at a high positive potential and thus avoid crevice corrosion. To test this idea powdered nickel metal and \( \text{NiO} \) were added to several commercially available coating materials. These were applied to the surface of \( \frac{1}{2} \) square specimens of C.P. titanium with a hole drilled in the center. These were then bolted together with titanium nuts and bolts so that the coating was in the crevice between the specimens. These specimens were placed in boiling saturated NaCl solution. The solutions were kept saturated with chlorine gas. At the end of three weeks the specimens were removed and examined.

Figure 5 is a photograph showing the appearance of the specimens after exposure and removal of the coatings. The control specimens which had no coating suffered severe crevice corrosion while all of the coated specimens showed no evidence of attack.

Further evidence in support of the theory that Ni or Mo ions in the crevice will suppress crevice corrosion of titanium is provided by an experiment in which specimens of 316 stainless steel were bolted to Ti-50A specimens to form sandwiches as previously described. A total of eight pairs of test specimens were prepared. Two sets had nothing in the crevice between the specimens. The

Fig. 5. Appearance of specimens after exposure and removal of coatings.
other six were all coated with Dow Corning Silastic RTV-732 in the area of the crevice. NiO was added to the Silastic used on two specimens. MoO₃ was added to two others and the remaining two served as controls with no additives.

Severe crevice corrosion of the titanium specimens occurred in the sandwiches that were coated with Silastic with no additives while the uncoated specimens and the ones with NiO and MoO₃ added showed no evidence of attack. 316 stainless steel contains both Mo and Ni as alloying ingredients. It appears that sufficient ions dissolved from the 316 stainless steel to keep the titanium passive where no coating was used. In the case where the Silastic coating with nothing added was used severe attack occurred because the coating served to isolate the titanium from the 316 stainless steel and formed a crevice from which Ni and Mo ions were excluded. The coatings to which NiO and MoO₃ were added provided sufficient ions in the crevice to passivate the titanium.

Summary

Electrochemical polarization measurements indicate that the presence of dissolved oxygen or chlorine in a brine solution shifts the corrosion potential of titanium in the positive or passive direction so that in general the presence of oxygen or chlorine in the solution tends to suppress corrosion.

It is postulated that crevice corrosion results when the oxygen or chlorine in a crevice is consumed faster than it diffuses into the crevice from the bulk solution. As a result the potential of the metal in the crevice becomes more negative than the potential of the metal exposed to the bulk solution. This sets up an electrolytic cell with the metal surfaces in the crevice acting as the anode and the adjacent metal outside the crevice acting as the cathode. Metal dissolves at the anode under the influence of the resulting current and hydrogen is generated at the cathodic areas.

It has been observed that the addition to the crevice solution of small amounts of multivalent ions of such metals as iron, copper, nickel and molybdenum act as cathodic depolarizers and tend to shift the corrosion potential of the titanium exposed to the solution back in the positive direction, thus counteracting the effect of the oxygen or chlorine depletion and effectively preventing crevice corrosion.

These observations lead to the idea that multivalent metal ions supplied only in the crevice might maintain this area at a high positive potential and thus avoid crevice corrosion. Crevice corrosion tests in which coatings containing suitable metallic ions were applied to the area of the crevice confirm the effective-
ness of this solution to the problem of crevice corrosion of titanium.

References


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