

Communication—The galvanic effect on the under-deposit corrosion of titanium in chloride solutions

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Abstract

Solid deposits are commonly present during industrial operations. The corrosion behavior of solid-covered Ti-2 in a solid-covered/uncovered galvanic cell was studied here. Corrosion is maximized at a specific deposit thickness: not too thin and not too thick. It initiated when the deposit layer thickness was 4 cm, and became more severe as the thickness increased to 6 cm. However, a further increase in the thickness resulted in significant mass transfer resistance in the corrosion process and did not result in exacerbated corrosion. Under-deposit corrosion of titanium in a neutral chloride solution manifested the autocatalytic characteristics of occluded cell corrosion.

Introduction

Solid deposits are reported to cause or accelerate corrosion of the metal beneath or around deposits. This phenomenon is generally referred-to as under-deposit corrosion (UDC)¹⁻³. UDC has frequently been implicated in high corrosion rates and loss of containment of pipeline equipment³⁻⁵. Solid deposits on the surface result in an occluded region, where the local solution chemistry may change and underlying metal may show different corrosion behavior from that in the bulk solution. This results in a galvanic corrosion cell between the metallic portion under the deposits and the portion without deposits. The resultant galvanic effect can be significant and is reported to be an important mechanism of UDC^{2, 6-8}.

Titanium and its alloys are considered to be highly corrosion resistant even in the presence of chlorides⁹, and they are important structural materials used for

hydrometallurgical vessels, nuclear fuel waste containers, desalination plants and chemical processing equipment where solids deposition is frequently encountered⁹⁻¹⁰. Titanium is susceptible to crevice corrosion, where the occluded region is usually created by narrow fissures or gaps^{10, 11}. UDC shares similarities with crevice corrosion—they both form an occluded region—and it may also be a threat to the integrity of titanium. However, UDC of titanium has not been previously investigated. Such an investigation is necessary considering the potential for corrosion and, ultimately, the possibility of catastrophic failure, which might occur, for example, in pressure vessels. This work investigates titanium corrosion where partial deposition of solids on the surface occurs. Specifically, the galvanic effect on deposit-covered titanium in the deposit-covered/uncovered titanium galvanic cell is studied.

Experimental

A conventional galvanic coupling technique was employed, where a small working electrode (WE) in the occluded (solid-covered) region and a large counter electrode (CE) exposed to the external environment (uncovered region) are separated. A WE and CE of the same composition were cut from Ti-2 (C 0.012, N 0.008, O 0.120, and Fe 0.120 wt.%; H 17 ppm; and Ti as the balance) shim stock with 0.13 mm thickness. The WE was cut into a 1 × 1 cm flag shape and the CE was a 10 × 5 cm flag (Figure 1(a)): their area ratio was approximately 1:50. The flags and flag poles were both Ti-2. The flagpoles of the flag electrodes were electrically connected to the potentiostat leads. The use of flag samples avoids crevice corrosion concerns that may arise with epoxy-mounted or PTFE holder samples. 0.27 M NaCl was used and prepared with DI water and Crystalline/Certified ACS NaCl. The test solution was vigorously aerated by transferring it between two beakers in air five times.

A 1-L, cylindrical cell with a separate lid and a water jacket was used for the experiments. The lid and the vessel were tightly connected by a clamp to seal the cell from the ambient air. Electrodes could be secured to ground glass joints on the lid. Laboratory-grade silica particles ($0.99 \text{ m}^2 \cdot \text{g}^{-1}$, $d_{0.5} = 20.4 \text{ }\mu\text{m}$, VWR) were used to simulate the deposits that may occur industrially. The silica was contained in a separate beaker and saturated with the test solution before being introduced to the test cell. The WE was vertically inserted into silica to a depth of 2–8 cm to simulate the solid-covered portion; the large CE

was located outside the beaker, but in a common electrolyte to simulate the uncovered portion (Figure 1(b)). The WE and CE were connected via the zero-resistance ammeter mode of the potentiostat, and the corrosion circuit is shown in Figure 1(c). The current flowing between the WE and CE, and the galvanic potential of the coupled electrodes were measured as temperature was increased. The temperature was set initially to 55°C and then increased stepwise at a rate of 5°C every 48 h until reaching the initiation temperature or up to 90°C, whichever came first. Before the test, the WE and CE were activated in 0.3 M sulfuric acid solution at 70°C for 30 min to dissolve any existing oxide film, then rinsed with DI water for 30 seconds and immediately introduced to the test solution. An Ag/AgCl (4 M KCl) reference electrode within a Luggin probe was used. The tip of the Luggin capillary was placed approximately 3mm away from the WE; all potentials are quoted with respect to this reference electrode (0.197 V vs. standard hydrogen electrode). Experiments were conducted with an AMETEK Potentiostat/Galvanostat VersaSTAT 4. All tests were repeated only twice due to the long test duration.

Results and Discussion

At the beginning, both the WE and CE underwent passivation. When one Ti-2 portion was covered by 2 cm of solids, the galvanic potential rose steadily as the temperature was increased to 60°C, and slowly leveled off toward a potential of ~0.35 V as the temperature was increased to 90°C (Figure 2(a)). The galvanic current flattened out with its magnitude gradually decreasing to a few nA; the initially negative magnitude was due to the anodic dissolution and eventual passivation of the large counter electrode¹⁰. The high and stable potential, and small current magnitude indicate that corrosion was not initiated in the galvanic cell. Visual examination of the sample after the test did not show any morphological changes consistent with corrosion attack.

When the deposit thickness was 4 cm, the galvanic potential stabilized at 0.23 V, and current leveled off to a negligible amount (~nA) as the temperature was increased up to 85°C (Figure 2(b)). However, at 90°C, the potential showed an obvious decrease to a local minimum of ~0.16 V, and the current simultaneously increased to a maximum of 0.58 μ A—this signified corrosion initiation of the underlying, deposit-covered, titanium. The corrosion propagation did not last long (~24 hours) before the potential started to increase

and the current decreased, indicating the repassivation process.

Under a 6 cm-deposit layer, UDC was initiated when the temperature reached 75°C (Figure 2(c))—potential showed an obvious drop to 0.1 V, and the current increased to 0.7 μA . In addition to the lower initiation temperature, the larger galvanic current and lower galvanic potential indicated corrosion under a 6-cm layer should be more severe than under a 4-cm layer. When the deposit layer thickness was increased to 8 cm, the corrosion was still initiated at 75°C as indicated by the potential drop (Figure 2(d)), while the galvanic current remained very low ($\sim\text{nA}$), indicating slower corrosion. After the test, the titanium samples with deposit thickness 4–8 cm showed signs of UDC attack (Figure 2(b-d)) due to surface color changes (brownish) and visible pitting, as shown in Figure 3(a).

In the neutral solution used here, titanium corrosion is not normally expected^{10,12}. UDC initiation on Ti-2 in the silica-covered/uncovered galvanic cell is consistent with deoxygenation-acidification theory based on crevice corrosion studies (Figure 3(b))^{11,13-15}. As oxygen depletes within the occluded region, oxygen reduction (cathodic reaction) occurs mainly outside the occluded region due to the restricted mass transfer; thus, metal dissolution (anodic reaction) is the dominant reaction in the crevice (or under the deposit). This results in an increase in metal cation concentrations and local acidification due to cation hydrolysis in the occluded region. The drop in solution pH and Cl^- accumulation (to maintain electrical neutrality) lead to an increasingly aggressive solution where active corrosion takes place¹⁴⁻¹⁸. Because of these autocatalytic characteristics, occluded cell corrosion is one of the most insidious forms of metal failure. Its manifestation in UDC of Ti is important for industrial operations.

The corrosion of solid-covered Ti-2 is clearly dependent on the thickness of the deposit layer. Galvanic corrosion occurred as the layer thickness increased to 4 cm and became more severe as the thickness increased to 6 cm. The thicker deposit layer tends to make for a more occluded region, where oxygen depletion and local solution chemistry change is more rapid and significant as revealed by crevice corrosion studies¹⁶. However, thicker deposits, such as the 8 cm condition tested here, also result in an increased mass transfer resistance (R_{deposits} in Figure 1(c)), which then inhibits the corrosion process. This explains Figure 2(d), where corrosion did not become more severe when the deposit layer was increased to 8 cm. Thus, it

appears that galvanic corrosion reaches a maximum at an intermediate thickness: when the deposit is thin (<2 cm) it allows oxidant ingress to the metal surface, enabling passivation; as the deposit gets thicker (4 to 6 cm), oxidant ingress is suppressed and the metal corrodes due to acidification. Finally, when the deposit is even thicker (8 cm) it cuts off most of all mass transfer and reduces corrosion by inhibiting the ionic path. This thickness will be highly situationally-dependent and should be further studied.

Conclusions

The solid-covered Ti-2 in the solid-covered/uncovered galvanic corrosion cell was susceptible to an autocatalytic acidification corrosion process in 0.27 M NaCl. UDC of Ti-2 initiated as the deposit layer increased to 4 cm, and became more severe and more susceptible as the layer increased to 6 cm. However, further increase of the layer thickness to 8 cm suppressed the corrosion because of the limited ionic path for the corrosion process. There is a specific deposit thickness that maximizes corrosion of the solid-covered portion of solid-covered/uncovered galvanic cells.

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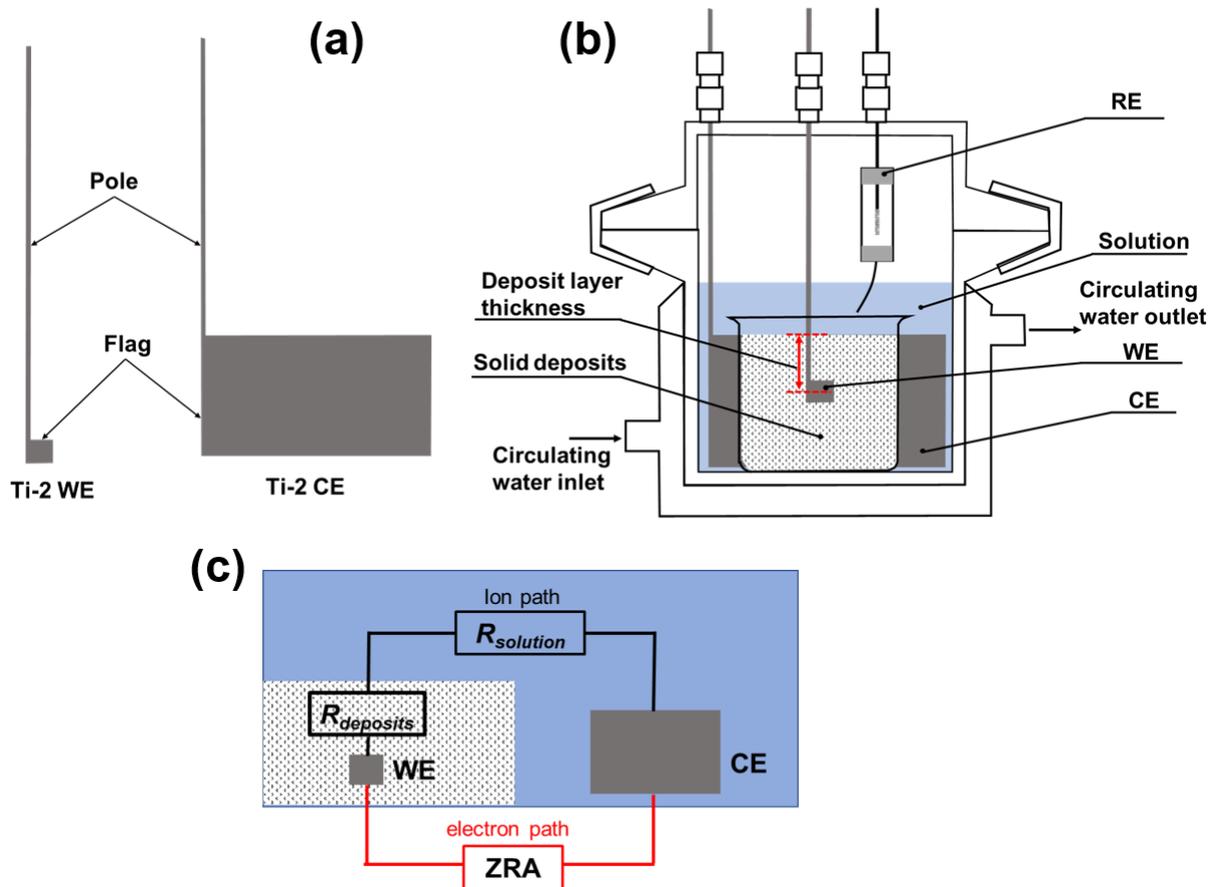


Figure 1 (a) schematic of Ti-2 electrodes, (b) setup showing a beaker holding the deposits and the WE, which was immersed in the common electrolyte (the deposit layer thickness was measured from the surface of the deposit to the center line of the WE; due to the vertical insertion of the sample, the layer thickness was not uniform around the WE surface), and (c) schematic of the corrosion circuit in the deposit-covered/uncovered galvanic cell

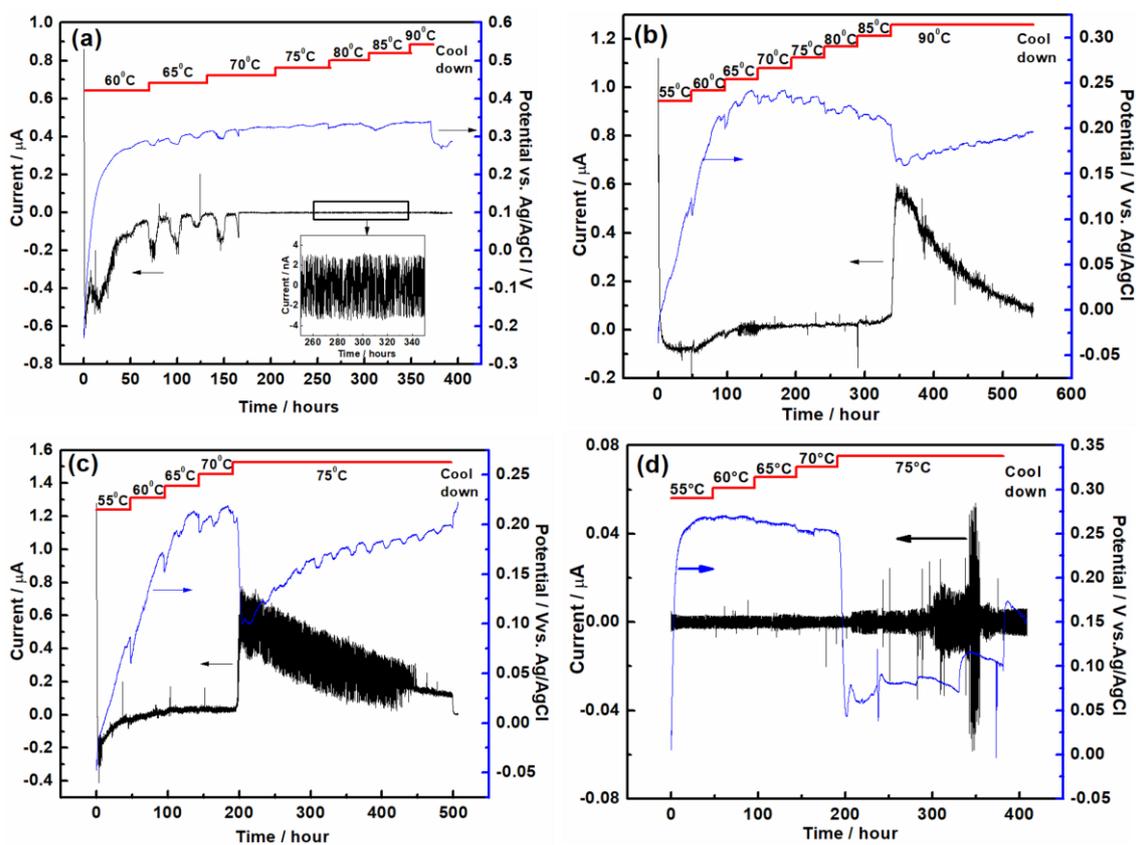


Figure 2 Potential and current of solid-covered Ti-2 in the solid-covered/uncovered cell as a function of temperature in 0.27 M NaCl solution when the deposit thicknesses was (a) 2 cm, (b) 4 cm, (c) 6 cm, and (d)

8 cm

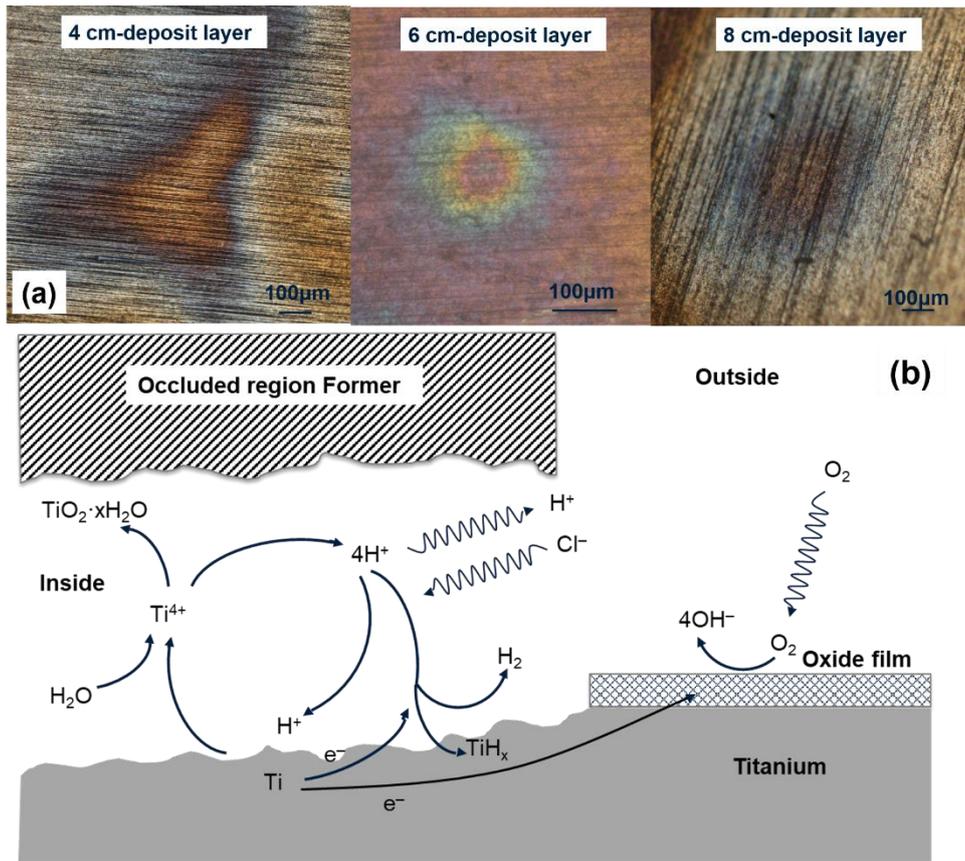


Figure 3(a) Pits on the solid-covered Ti-2, and (b) schematic representation of the corrosion initiation on the solid-covered Ti-2