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Corrosion of titanium alloys in high temperature near anaerobic seawater

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ABSTRACT

Grades 2, 5 and Grade 7 were investigated in near anaerobic (<1 ppm oxygen) seawater up to 200 °C with and without CO₂. All three grades were found to resist stress corrosion cracking and pitting corrosion. Grades 2 and 5 suffer crevice corrosion at temperatures 80 °C and 200 °C respectively. In the presence of CO₂ Grade 5 becomes more vulnerable to crevice corrosion, with attack starting at 80 °C with preferential dissolution of the beta phase. An analysis of the threat of hydrogen induced cracking leads to the conclusion that this was not a likely threat to any of the Ti alloys investigated.

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1. Introduction

Materials of choice for offshore structures and the marine industry have increasingly been moving toward light-weight materials. One of the most promising family of light-weight materials are titanium alloys, but these are not immune to corrosion and could be vulnerable in low-oxygen high-temperature environments at deepsea well-heads.

During the early 1980s there was interest in using titanium canisters for deepsea disposal of high level radioactive waste, which gave rise to research into its behavior in high temperature, high pressure and low O₂ environments [1,2]. However, the dumping of nuclear waste at sea was banned in the late 1980s, after which there was little interest in use of Ti in deepsea applications. In the last decade the exploration for new sources of oil and minerals has moved into deeper waters, resulting in a demand for materials that offer high strength-to-weight ratios for applications such as risers, making Ti alloys an obvious choice. However, despite titanium reputation for corrosion resistance it is vulnerable under anaerobic conditions, especially at high temperatures, if the passive oxide film cannot be maintained [3,4]. Unfortunately, the conditions at a deepsea well-head, where temperatures can exceed 120 °C and oxygen levels can be below 1 ppm, are those that could lead to the

loss of the passive film, especially in regions where crevices form [5]. The situation is likely to be even worse if localized acidity is produced due to the presence of CO₂.

As long as the passive film stays intact, such that the corrosion rate is low, the corrosion potential of a titanium alloy in an anaerobic environment can be expected to lie on or just below the hydrogen equilibrium potential. From the Pourbaix diagram for titanium (Fig. 1) it can be seen that, unlike stainless steels, Ti can potentially suffer crevice corrosion in anaerobic seawater (pH 8.2), i.e., there is a large corrosion regime below the hydrogen equilibrium line [6].

Increasing the temperature causes the hydrogen equilibrium line to increase its slope according to the Nernst equation:

$$E = 0 - \frac{2.303RT}{F} \text{pH} - \frac{2.303RT}{2F} \log [P_{\text{H}_2}]$$

Furthermore, the equilibrium constant that controls the concentrations of protons and hydroxyl ions in water (pK_w) increases with temperature, such that at 200 °C the pH of distilled water is 5.66; note that this is still a neutral solution as there are equal concentrations of H⁺ and OH⁻ ions, and that it is simply a result of K_w having increased to 10^{-11.3} from its 298 K value of 10⁻¹⁴ [7]. Table 1 shows the expected pH and calculated hydrogen equilibrium potentials in distilled water for a range of temperatures, with the pressures being taken from steam tables. The pH and hydrogen equilibrium potentials given in Table 1, essentially give the coordinates on the Pourbaix diagram where a piece of titanium in

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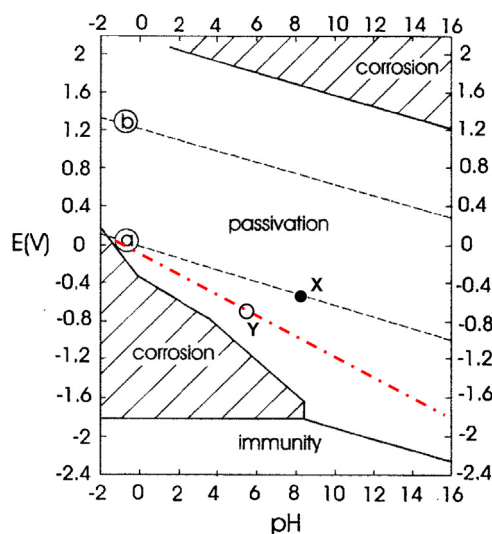


Fig. 1. Pourbaix diagram for titanium [6]. The dot-dash line shows the calculated hydrogen equilibrium potentials at 200 °C. When combined with the temperature dependence of pK_w , the position of the hydrogen equilibrium potential in seawater moves from point X (solid circle) at 25 °C to point Y (open circle) at 200 °C. In addition the solubility of Ti^{3+}/TiO_2^{2+} ions increases with temperature, such that the anaerobic corrosion zone will expand to the right and could encompass the point Y.

anaerobic distilled water can be expected to be found as long as it remains in the passive state. Sufficient data is not available to make similar calculations for seawater, where the situation might be further complicated by temperature dependence of the solubility of carbonate and bicarbonate salts, but it is unlikely to be radically different from the case of distilled water. A further effect of increasing the temperature is that the solubility of Ti^{3+}/TiO_2^{2+} will increase, expanding the anaerobic corrosion regime in the Pourbaix diagram. This further reduces the gap between the corrosion regime and the expected open-circuit conditions of titanium (i.e., the pH and hydrogen equilibrium potentials in Table 1), and thereby markedly increases the likelihood of crevice corrosion as illustrated in Fig. 1. Indeed it is even possible that at some temperature the corrosion regime could encompass the expected open-circuit conditions, such that the titanium would lose its passive film and undergo general corrosion. It is perhaps worth noting that pK_w reaches a minimum of 11.2 at 250 °C after which it starts to rise again as the water becomes supercritical.

Another potential vulnerability of a titanium alloy in high temperature anaerobic seawater is that any hydrogen evolved on its surface could enter its matrix and form a hydride leading to embrittlement and hydrogen induced cracking (HIC) [8–11]. The present paper will therefore present the results of investigations, along with an analysis of the available literature, into the corrosion behavior of a range of titanium alloys in artificial anaerobic seawater with and without CO_2 saturation over the temperature range 60–200 °C.

Table 1
Influence of temperature and pressure on the pH and calculated hydrogen equilibrium potential in distilled water. The pH values taken from Bandura and Lvov [7].

| Temperature (°C) | pH | V vs. SHE | V vs. Ag/AgCl/0.1 M KCl |
|------------------|-----|-----------|-------------------------|
| 25 | 7.0 | −0.415 | −0.682 |
| 65 | 6.5 | −0.435 | −0.662 |
| 100 | 6.1 | −0.453 | −0.641 |
| 125 | 5.9 | −0.484 | −0.643 |
| 160 | 5.8 | −0.531 | −0.647 |
| 200 | 5.7 | −0.592 | −0.653 |

2. Experimental

The titanium alloys investigated were commercial Grade 2 (UNS R50400), Ti6Al4V Grade 5 (UNS R56400), the 0.2 wt% Pd containing alloy Grade 7 (UNS R52400) and newly developed alloys based on the metastable beta alloy Grade 19 (UNS R58640) but with additions of the rare earth yttrium element (0–1 wt%) that were fabricated in-house via vacuum arc melting. Grade 19 is used in some offshore applications due to its high yield strength >760 MPa and the Y addition refines the grain structure leading to increased strength and plasticity [12,13]. Unfortunately, limitations in metallurgical process facilities render it difficult to produce any suitable Grade 19 specimens for the crevice and U-bend tests, so these alloys were only used in the electrochemical experiments. The compositions of the Ti alloys used are shown in Table 2.

The test environment was artificial seawater (pH 8.2) fabricated in-house in compliance with ASTM D1141-98 (Table 3), which was deoxygenated with either N_2 or CO_2 for more than an hour immediately prior to the experiments with a blank of the gas left sealed inside the reaction chamber. This was a Hastelloy C-276 autoclave (Cortest Inc.) with the temperature controlled to ± 1 °C. Both the crevice and U-bend assemblies were immersed in the seawater for 7 days.

For the crevice corrosion tests the specimen dimensions were $50 \times 50 \times 1$ mm. The surfaces were ground to a 600-grit before cleaning with acetone/ethanol and deionized water. Each crevice former had 20 teeth of height 2.5 mm, the inside diameter to the teeth was 17 mm while the outside diameter was 22 mm. Crevice assemblies were designed according to ASTM G78-01, with one polytetrafluoroethylene (PTFE) crevice former on each side of the specimen (i.e., 40 teeth in contact with each specimen) and tightened to a torque of 3 Nm. The depth of the crevice corrosion was measured by either surface profilometer or cross sectioning.

The dimensions of the U-bend specimens were $90 \times 20 \times 1$ mm, with the surfaces polished to a 600-grit finish and cleaned with acetone/ethanol and deionized water. The U-bend assemblies were fabricated in accordance to ASTM G30-97 (Reapproved 2009), and their outer surfaces undergo a total strain of 5%.

All the electrochemical tests were conducted at 160 °C in the autoclave, the reference electrode was a Cortest Inc. designed high pressure Ag/AgCl/KCl_(0.1M) arrangement, with all potentials being quoted against this system (0.116 V vs. SHE at 160 °C). The Ti alloy test specimens were cut to a length of 10 mm from 8 mm diameter rods, with total surface area exposed to the electrolyte being 3.0 cm². The working electrodes were ground to a 600 grit finish, followed by cleaning in acetone/ethanol and deionized water. The counter electrode was a Pt/Nb alloy provided by Cortest Inc. The electrochemical tests consisted of: open-circuit potential (OCP) measurements over a period of 30 min; Tafel measurements conducted at a sweep rate of 0.17 mV s^{−1}; potentiodynamic polarization pitting tests from −1.0 V to a maximum of +2.0 V vs. Ag/AgCl/KCl_(0.1M) (or reverse at 1 mA cm^{−2}) at 2 mV s^{−1}, with the onset of pitting corrosion being assumed to occur when the current density reached a value of 0.01 mA cm^{−2}; and oxide reformation experiments, in which two potentiodynamic scans are performed to a potential of 0.7 V vs. Ag/AgCl/KCl_(0.1M) separated by a period of 2 h under open-circuit conditions with the second scan starting at the recorded OCP. As the thickness of the passive film on valve metals (such as Ti) is directly proportional to the positive potential limit of the first scan, any thinning that occurs during the time at open-circuit manifests itself as an early rise in the current density as the film reforms to its original thickness. If the anodizing ration is known potential at which the current density increases in the second scan can be directly related to the loss of passive film thickness [4]. Care needs to be taken in the interpretation of electrochemical data due to the semiconductor nature of the passive

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