PITTING CORROSION OF TITANIUM

IN HIGH TEMPERATURE HALIDE SOLUTIONS

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Introduction

Corrosion resistance of titanium is characterized by the tendency to be easily passivated, stable passivity over a wide range of potential and temperature, and insensitivity to detrimental effects of halide ions. Based on these properties, titanium is the best possible material of construction available for halide solutions. As shown by numerous reports and data on the behavior of titanium in halide solutions (1)-(6), however, there is a limitation to extensive use due to its tendency to suffer localized corrosion such as crevice or pitting in high temperature halide solutions.

Localized corrosion of titanium and its alloys in high temperature halide solution has recently been studied by several investigators (1)-(3) especially in relation to desalination plants. Posey and Bohlmann (1) studied electrochemical aspects of pitting corrosion of titanium and its alloys in high temperature salt solutions, and found that the critical potentials for pitting were greatly affected by temperature. By evaluating the corrosion resistance of titanium and its alloys to crevice corrosion in high temperature chloride solution, Griess(2) clarified that there is a close relation between resistance to nonoxidizing acid solution and to crevice corrosion. Feige and Murphy(3) reviewed the corrosion evaluation studies and presented a diagram in which the regions of immunity and localized corrosion of titanium and its alloys are defined with temperature and concentration of NaCl.

In recent possible applications other than desalination plants, for example, chemical equipment in which liquid phase oxidation of...
organic compounds is carried out at high temperature under the presence of halide ions, more detailed electrochemical data on pitting corrosion of titanium are also required. The present study has been made of the influence of various environmental factors such as temperature, pH of the solution, additive anions and concentration of halide ions, on the pitting corrosion of commercially pure titanium in bromide and chloride solutions.

Experimental

Electrochemical measurements were carried out in an autoclave equipped with working and counter (platinum) electrodes, and a liquid junction for external S.C.E. reference electrode (Fig. 1). Electrochemical studies were conducted from room temperature to 250°C, and the temperature was controlled within ±3°C in most cases. Specimens for measurements were cut from commercially pure titanium sheet, polished up to No. 800 emery paper, and pickled in HNO₃-HF solution. Since titanium is very sensitive to crevice corrosion, specimens were cut in a shape shown in Fig. 2 so as to avoid forming crevices at any part of the specimen immersed in solution. So-called critical potentials for pitting and corrosion were measured in NaCl and NaBr solution in a wide range of temperature, pH and concentration of halide ions. The electrolytes for most experiments were 0.53 N NaCl (3%) and 1 N NaBr, and they were prepared by reagent grade chemicals and deionized water. Purified argon gas was flowed through the electrolyte for deaeration prior to heating, and oxygenation was done by pressurizing with oxygen gas. As the critical potential in NaCl solution is usually more noble than the oxygen electrode potential, the titanium electrode was polarized anodically by use of a constant current source. In NaBr solution, on the contrary, the critical potential falls on less noble potentials, and so both a potentiostat and a constant current source were used for polarization.

Experimental Results

Temperature dependency of pitting potential

Temperature is one of the most important environmental factors affecting the critical potential for pitting of typical passive materials such as stainless steels and titanium in chloride solutions (1)(7)(8). Aluminum (9), on the contrary, is not so sensitive to temperature.

Fig. 3 shows the effect of temperature on the critical potential for pitting of titanium in 0.53 N NaCl and 1 N NaBr solutions. In chloride solution, the pitting potential drastically shifts in the active direction with increase of temperature up to about 130°C, but does not change so steeply at temperatures higher than 130°C. According to the previous study by Posey and Bohlmann (1), the pitting
Fig. 1. Autoclave assembly used for electrochemical measurements.
Fig. 2. Titanium electrode used for electrochemical measurements.

Fig. 3. Effect of temperature on critical potential for pitting in 0.53 N NaCl and 1.0 N NaBr.
potential of commercially pure titanium in 1 N NaCl shifts to 0 V S.C.E. at 220°C. The data obtained by the present study, however, showed that the critical potential still remained more noble than 1 V S.C.E. even at 250°C. This was confirmed by a preliminary test in which titanium immersed in aerated and oxygenated 0.5 - 1.5 N NaCl solutions at 250°C showed no pitting on free surfaces in spite of a corrosion potential more noble than 0.2 V S.C.E.

In bromide solutions, on the contrary, the critical potential does not change so sensitively as in chloride solution over the temperature range between room temperature and 250°C, and it is much more active in potential than that in chloride solution. This behavior is much different from that of stainless steels in which the critical potential in bromide solution is more noble than in chloride solution(8).

Effect of pH

The critical potentials for pitting were measured in 0.53 N NaCl solutions ranging in pH from 1 to 7 (adjusted by HCl) at 200°C. As shown in Fig. 4, the effect of increasing acidity in 0.53 N NaCl solution is to shift the critical potential in the active direction by about 0.2 V from pH 7 to pH 1.

Fig. 4. Effect of pH on critical potential for pitting in 0.53 N NaCl at 200°C.
Effect of halide ion concentration

The effect of increasing chloride ion concentration in acidic NaCl solution (pH = 3) was examined between 0.04 and 2 N at 200°C. The critical potential for pitting shifts in the less noble direction by about 0.1 V for a ten-fold change in concentration (Fig. 5). This value is comparable with the data obtained for aluminum (0.13 V) and 18-8 stainless steel (0.09 V).

The effect of bromide ion concentration, on the other hand, is four times as much as that of chloride ion. Fig. 6 shows the concentration dependency of critical potentials in NaBr solution at room temperature. The relations between critical potentials vs. S.C.E. in volts and concentration of halide ions are represented by the following equations:

\[ V_c = 1.4 - 0.10 \log Cl^- \text{ (at 200°C)} \]  
\[ V_c = 1.1 - 0.43 \log Br^- \text{ (at room temperature)} \]

Inhibitive effects of additive anions

It is well known that various anions when added to chloride solutions shift the critical potential for pitting to a noble value, improving resistance of materials to pitting corrosion (7). Dugdale and Cotton (10) showed that pitting corrosion of titanium in halide solutions is inhibited by addition of sulfate ion, and that titanium behaves as if it were in pure sulfate solution. They also determined the concentration of sulfate ion sufficient to inhibit pitting corrosion.

In the present study, the effects of various oxyanions such as \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), \( \text{CrO}_4^{2-} \), \( \text{PO}_4^{3-} \), and \( \text{CO}_3^{2-} \) in NaBr solutions were investigated at room temperature and 200°C. Fig. 7 shows the concentration of additive anions required for inhibition of pitting in NaBr solution ranging in concentration from 0.01 to 1 N. As shown in Fig. 7, they can be divided into three regions which were defined as non-inhibitive, weak-inhibitive and strong-inhibitive regions. Fig. 8 represents anodic polarization curves corresponding to these three regions. In the non-inhibitive region, an abrupt increase of anodic current occurred almost at the same potential as the critical potential measured in the solution without additive anion. In the weak-inhibitive region, however, a current maximum appeared immediately before the pitting corrosion initiated on the surface, where bromide ion discharged on the surface and the solution became colored by \( \text{Br}_2 \). The critical potential for pitting obtained by extrapolation was shifted in the noble direction by 0.5 V. With the increase of additive anions, a remarkable change in shape occurred in the anodic polarization curve, and pitting corrosion was completely inhibited (strong-inhibitive region). The current maximum was considerably lowered and the solution was not apparently colored. The concentration of
Fig. 5. Effect of chloride concentration on critical potential for pitting in 0.53 N NaCl at 200°C (pH = 3.0).

Fig. 6. Effect of bromide concentration on critical potential for pitting in 1.0 N NaBr at room temperature (pH = 6.5).
Fig. 7. Concentration of various oxyanions required to inhibit pitting as a function of \( \text{Br}^- \) concentration (room temperature). A: Non-inhibitive region; B: Weak-inhibitive region; and C: Strong-inhibitive region.
Fig. 8. Anodic polarization curves corresponding to non-inhibitive (0.5 N NaBr + 0.01 M Na₂SO₄), weak-inhibitive (0.5 N NaBr + 0.1 M Na₂SO₄), and strong-inhibitive (0.5 N NaBr + 0.5 M Na₂SO₄) regions, respectively.

Fig. 9. Effect of oxygenation on corrosion potential of titanium in 0.53 NaCl at 200°C and 250°C (dotted lines).
additive anions required to inhibit pitting corrosion strongly increases linearly with that of halide ions, but the boundary between weak- and non-inhibitive regions is not always straight.

The weak-inhibition hardly occurred at 200°C, and non-inhibitive and strong-inhibitive regions made directly a straight boundary which was consistent with that between weak- and strong-inhibitive regions at room temperature.

According to the boundary line between weak- and strong-inhibitive regions, efficiency of inhibition decreases in the order $\text{SO}_4^{2-} \rightarrow \text{NO}_3^- \rightarrow \text{CrO}_4^{2-} \rightarrow \text{PO}_4^{3-} \rightarrow \text{CO}_3^{2-}$.

**Effect of dissolved oxygen**

On using titanium as a structural material in oxygenated environments containing halide ions, it is important to know the effect of oxygenation, or dissolved oxygen, on the corrosion behavior of titanium. In the present study, the autoclave was pressurized prior to heating with oxygen up to 40 kg/cm$^2$ at room temperature, and the effect on the corrosion potential and critical potential for pitting was examined at 200 and 250°C. The corrosion potential of titanium was about -0.2 V S.C.E. in deaerated 0.53 N NaCl solution, and when naturally aerated, the potential was shifted in noble direction by about 0.4 V. As shown in Fig. 9, the rest potential of titanium moved to a still more noble value when the solution is oxygenated. The critical potential for pitting of titanium was not affected by oxygenation.

In chloride solution, the difference between pitting and rest potential of titanium remains more than 0.8 V even if the solution is oxygenated. This suggests that titanium is unlikely to suffer pitting corrosion on a free surface except in a highly concentrated solution. In high temperature bromide solution, on the other hand, pitting corrosion is quite possible even on a free surface.

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**References**