Corrosion Inhibition of Titanium in Acidic Media Containing Fluoride with Bixin

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Abstract: The bixin in acidic media were tested for corrosion inhibition of Ti in 0.5 N sulphuric acid and 0.1 N HCl solution at 30 to 40 °C temperature range by electrochemical methods. It reveals that bixin works as a corrosion inhibitor in halide media and protect the metals from the corrosion with great efficiency.

Keywords: Corrosion, Titanium, Galvanometric, pH metric.

Introduction

Titanium and its alloys are widely used in dentistry as prosthetic applications because of a high corrosion resistance and good conductivity. These valuable properties are caused by passive films that are rapidly formed in the body fluid environment. Recently mouth-rinses, toothpastes and prophylactic agents containing fluoride are utilizing to prevent the dental caries. However, decreasing the corrosion resistance of Ti in solution containing fluoride has been reported. The corrosion behaviors are related to the concentration of fluoride and the surrounding environment therefore, the surface reaction on Ti under the existence of fluoride is important to understand the corrosion in acidic environment.

The bixin exhibited excellent efficiency in acidic solution because of heterocyclic ring which contains N and O atoms in there structure, this ring induced grater adsorption of the metal surface. Due to adsorption phenomenon bixin shows grate on the ability of corrosion inhibition. Recently it has been used as inhibitor on the corrosion on stainless steel in phosphoric acid solution.

Experimental

The specimen plates of size 1 cm x 1 cm x 1 cm were used and immersed in acidic media, adaptable to the working electrode. The sample was mechanically cleaned with abrasive strips. The electrolyte reference used was Fusayama Meyer artificial saliva, the composition of this solution is KCl (0.4 g/L), NaCl (0.4g/L) calcium chloride (0.906 g/L),
sodium dihydrogen phosphate (0.69 g/L) sodium sulphide (0.005 g/L) and urea (1 g/L). The pH was measured with the glass electrode. The pH of this solution is 7.1 corresponding to first tested media. The second media used has the same contents as the first, but the pH is lower than it. The third media was identical to the reference media but enriched with fluoride ions with a concentration 0.5% and the last medium is containing fluoride at pH 2 at different concentration of bixin.

For electrochemical step, we used a glass electrode, with the thermostat at 40 °C. The three electrodes system was used, with a saturated calomel electrode, platinum plat counter electrode and working electrode (specimens test) connected to a potentiostat. The electrochemical analysis involved, measuring of linear polarization resistance ($R_p$), potentiodynamic polarization and AC impedance in different media.

**Statistical analysis**

The corrosion parameter, included $I_{corr}$ and $R_p$ were analyzed using one –way ANOVA for analyzing the factor of NaF or bixin concentration in 0.1% containing media, the results of $I_{corr}$ and $R_p$ values of the test in presence of fluoride had a statically significant influence on the value of $R_p$ ($p< .00005$) and $I_{corr}$ ($p<2.1090 \times 10^{-8}$).

**Results and Discussion**

The electrochemical parameters determined from the polarization curve (Figure 1) are given in Table 1. The corrosion current density of Ti increases with the increasing of pH, from 0.0127 mA/cm$^2$ in reference media to 0.445 mA / cm$^2$ in pH 2 medium and 2.0 mA/cm$^2$ in media containing fluoride.

The result shows that, fluoride ions cause the breakdown of the protective passivation layer, so it’s necessary to church inhibitor that suppressed this corrosion.

**Table 1.** Summary of electrochemical parameters for titanium in different media.

<table>
<thead>
<tr>
<th>Medium/Electrolyte</th>
<th>$I_{corr}$ mA/cm$^2$</th>
<th>$R_p$ $\Omega$cm$^2$</th>
<th>E mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saliva pH=7.1</td>
<td>0.0127</td>
<td>5249</td>
<td>-791.6</td>
</tr>
<tr>
<td>Saliva pH=3</td>
<td>0.445</td>
<td>200.3</td>
<td>-1600</td>
</tr>
<tr>
<td>Saliva pH=3+fluoride</td>
<td>2.0</td>
<td>55.7</td>
<td>-1697.7</td>
</tr>
</tbody>
</table>

**Figure 1.** Polarization curve after 1 h of immersion in media saliva pH 2 with and without fluoride.
The electrochemical parameters determined from the polarization curves (Figure 2) are given in Table 2.

![Polarization curves](image)

**Figure 2.** Polarization curves after 1 h of immersion in fluoride medium saliva pH 2 with fluoride for Ti.

**Table 2.** Summary of electrochemical parameters for grade-2 in fluoridemedia at different concentration of bixin

<table>
<thead>
<tr>
<th>Concentration of bixin</th>
<th>I_corr (mA/cm²)</th>
<th>R_p Ωcm²</th>
<th>E mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.013</td>
<td>55.7</td>
<td>-791.6</td>
</tr>
<tr>
<td>10⁻⁵ M</td>
<td>0.5445</td>
<td>164.3</td>
<td>-1543</td>
</tr>
<tr>
<td>10⁻³ M</td>
<td>0.155</td>
<td>432.34</td>
<td>-1097.7</td>
</tr>
</tbody>
</table>

The corrosion current density of Ti decreases with the increasing concentration of bixin, from 2.013 mA/cm² in reference medium at pH 2 containing fluoride 0.5% to 0.059 mA/cm² in 10⁻¹ concentration of bixin medium. The results showed that bixin revealed a good corrosion inhibitor. The efficiency depends on the concentration of bixin.

Impedance spectroscopy study was performed in order to confirm the results obtained with polarization tests. Figure 3 shows the impedance diagrams recorded for Ti in different medium to examine the concentration of bixin effect. In case fluoride medium at pH 2 the impedance curve is in the form of a half-circle which can be attributed to electron transfer reaction step. The diameter of circle of circle increased with increasing the concentration of bixin. However, at concentration 10⁻¹ M of bixin, the diagram curve is in the form of three-circle corresponding the formation the three-dimensional film on the surface that suppressed corrosion.
Figure 3. Electrochemical impedance spectra for Ti in fluoride media at pH 2 + Bixin.

Conclusion
Behavior of Ti in a solution containing fluoride and bixin were studied electrochemical properties, surface analysis potentiometry and pH. The results are summarized as following:
1. The corrosion resistance of Ti specimens’ solution containing fluoride decreases in comparison with that in a solution not containing fluoride. Adding of bixin to the solution resulted in preventing the corrosion of Ti.
2. The rate of corrosion on Ti in acidic solution of saliva was clearly lower than that in the solution containing fluoride at pH 2.

From these results, the effects of bixin are not only the protection of Ti from fluoride attack but also the suppression of dissolution of Ti via formation of bixin films. These effects evidently suppress the corrosion of Ti by fluoride.

References