Corrosion behaviour of SS 316 L in artificial saliva in presence of electral

Corrosion resistance of three metals namely, SS 316L, mild steel (MS) and mild steel coated with zinc (MS-Zn) has been evaluated in artificial saliva in the absence and presence of electral. Potentiodynamic polarization study and AC impedance spectra have been used to investigate the corrosion behaviour these metals. The order of corrosion resistance of metals in artificial saliva, in the absence and also in the presence of electral was SS 316L > MS > MS-Zn.

Keywords: Artificial saliva, corrosion, metals, electral, dentistry, oral hygiene

INTRODUCTION

In dentistry, metallic materials are used as implants in reconstructive oral surgery to replace a single tooth or an array of teeth, or in the fabrication of dental prostheses such as metal plates for complete and partial dentures, crowns, and bridges, essentially in patients requiring hypoallergenic materials. Due to its mechanical properties, good resistance to corrosion in biological fluids and very low toxicity, titanium was the most commonly selected material for dental implants and prostheses. Corrosion of metallic implants was of vital importance, because it can adversely affect the bio compatibility and mechanical integrity of implants. Many metals and alloys have been used in dentistry. Their corrosion behaviour in artificial saliva have been investigated. Influence of pH and corrosion inhibitors such as citric acid, sodium nitrate and benzotriazole on the tribocorrosion of titanium in artificial saliva has been investigated [1]. Five non-precious Ni-Co based alloys have been analyzed with respect to their corrosion behaviour in artificial saliva [2]. The effect of eugenol on the titanium corrosion in artificial saliva enriched with eugenol at different concentrations has been investigated by [3]. The corrosion resistance of the commercial metallic orthodontic wires in simulated intra-oral environment has been evaluated by Ziebowicz et.al. [4].

RESULTS OF CORROSION RESISTANCE TESTS OF THE CRNi, NiTi and CuNiTi wires showed comparable data of parameters obtained in artificial saliva [4]. The effects of multilayered Ti/TiN or single-layered TiN films deposited by pulse-biased arc ion plating (PBAIP) on the corrosion behaviour of NiTi orthodontic brackets in artificial saliva have been investigated [5]. Rajendran et al., have studied the corrosion behaviour metals in artificial saliva in presence of spirulina powder [6]. Corrosion behaviour of metals in artificial saliva in presence of D-glucose has been investigated [7].

The present work is undertaken

To study the corrosion behaviour of three metals, namely, mild steel, mild steel coated with zinc and SS316L in artificial saliva, in the absence and presence of electral, by polarization study and AC impedance spectra. Corrosion parameters such as corrosion potential, corrosion current, linear polarization resistance, charge transfer resistance and double layer capacitance have been derived from these studies. Electral is an oral rehydration salt. It is dissolved in water and taken orally. The main objective of the present study is to investigate how the oral intake of an aqueous electral solution affects the orthodontic wires used in dentistry. Hence the corrosion behaviour of three metals, in artificial saliva, in presence of electral is studied. The composition of commercially available electral is given in Tables 1 and 2. This electral powder is used in the present study.

Table 1: Composition of Electral Each Sachet (4.40g)

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride IP</td>
<td>0.52 g</td>
<td></td>
</tr>
<tr>
<td>Potassium Chloride IP</td>
<td>0.30 g</td>
<td></td>
</tr>
<tr>
<td>Sodium Citrate</td>
<td>0.58 g</td>
<td></td>
</tr>
<tr>
<td>Dextrose anhydrous</td>
<td>2.70 g</td>
<td></td>
</tr>
<tr>
<td>Excipients Qs</td>
<td></td>
<td></td>
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</table>
Table 2: Concentration of Electrolytes present in AS

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>MOs mole/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>75</td>
</tr>
<tr>
<td>Potassium</td>
<td>20</td>
</tr>
<tr>
<td>Chloride</td>
<td>10</td>
</tr>
<tr>
<td>Citrate</td>
<td>10</td>
</tr>
<tr>
<td>Dextrose</td>
<td>75</td>
</tr>
<tr>
<td>Total Osmolarity</td>
<td>24</td>
</tr>
</tbody>
</table>

MATERIALS AND METHODS

Three metal specimens, namely, mild steel, mild steel coated with zinc (commercial) and SS316L were chosen for the present study. The composition of mild steel is (wt%) 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron [8]. The composition of SS316L is (wt%): 18 Cr, 12 Ni, 2.5 Mo, <0.03 C and balance iron [9]. The metal specimens were encapsulated in Teflon. The surface area of the exposed metal surface was 0.0875 cm². The metal specimens were polished to mirror finish and degreased with trichloroethylene. The metal specimens were immersed in Fusayama Meyer artificial saliva [3], whose composition is: KCl (0.4 g/l), NaCl (0.4 g/l), CaCl₂·2H₂O (0.906 g/l), NaH₂PO₄·2H₂O (0.690 g/l), Na₂S·9H₂O (0.005 g/l), urea (1 g/l). The pH of the solution was 6.5. [10]

In electrochemical studies, the metal specimens were used as working electrodes. AS was used as the electrolyte. The temperature was maintained at 37 ± 0.1°C.

Commercially available electral powder (composition given in Tables 1 and 2) was used in this study. 0.5 g of electral was dissolved in 1 litre of artificial saliva.

Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was mild steel coated with zinc SS 316 L. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (Ecorr), corrosion current (Icorr) and Tafel slopes (anodic = bₐ and cathodic = bₐ) were calculated from Nyquist plots. Impedance, log(z/ohm) values were calculated from bode plots; The equivalent circuit diagram is shown in Scheme 1.

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell setup was also the same. The real part (Z’) and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (Rt) and the double layer capacitance (Cdl) were calculated.

RESULTS AND DISCUSSION

Analysis of potentiodynamic polarization curves

Corrosion behaviour of metals in artificial saliva. The corrosion parameters of various metals such as, mild steel, zinc coated mild steel and stainless steel 316L (SS), immersed in artificial saliva (AS) are given in Table 2. The potentiodynamic polarization curves are shown in Figs. 1 to 3.

![Figure 1. Polarization curves of MS immersed in various test solutions: a) AS, b) AS + electral](image1)

![Figure 2. Polarization curves of MS-Zn immersed in various test solutions: a) AS, b) AS + electral](image2)

Scheme 1. Equivalent Circuit Diagram: $R_s$ – Solution resistance, $R_t$ – Charge transfer resistance, $C_{dl}$ – Double layer capacitance
When mild steel is immersed in artificial saliva (AS), the corrosion potential is -657 mV vs SCE (Fig.1a). The linear polarization resistance (LPR) is $2.06 \times 10^4$ ohm cm$^2$ and the corrosion current ($I_{corr}$) is $1.98 \times 10^{-6}$ cm$^2$.

When zinc coated mild steel is immersed in AS, the corrosion potential shifts to the cathodic side (Fig.2a). The LPR value increases to $4.34 \times 10^4$ ohm cm$^2$ and the corrosion current decreases to $9.98 \times 10^{-7}$ cm$^2$. These observations indicate that zinc coated mild steel is more corrosion resistant than mild steel itself. A protective layer is formed on the metal surface.

In the case of mild steel coated with zinc, the cathodic Tafel slope is $187$ mV/decade and the anodic Tafel slope is $218$ mV/decade. These values suggest that during anodic polarization, the rate of change of corrosion current with potential is high, and it is less during the cathodic polarization.

When SS 316L is immersed in AS, the corrosion potential is shifted to the noble side (-385 mV vs SCE). This suggests that a protective film is formed on the metal surface, when it is immersed in AS. The LPR value is very high $5.52 \times 10^6$ ohm cm$^2$. The corrosion current decreases to a great extent. (8.55 x $10^{-9}$ cm$^2$). The values of Tafel slopes ($b_a = 430$, $b_c=145$ mV/decade) indicate that the rate of change of current with potential is high during anodic polarization than during cathodic polarization. During cathodic polarization, current remains constant over a potential range.

A comparison of LPR values and corrosion current values of the three metals investigated reveals that SS 316L is a better candidate to be used in dentistry.

Corrosion behaviour of metals in artificial saliva containing electral

Mild steel (MS): When mild steel was immersed in AS, containing electral, the corrosion potential was shifted to the cathodic side (when compared with the behaviour of mild steel in AS) (Fig.1b). The cathodic Tafel slope ($b_c$) value was higher than that of the anodic Tafel slope value. This indicates that the change of current with the change of potential was high in the anodic region than in the cathodic region. This is due to the formation of a protective fill on the anodic sites of the metal surface. This prevents the corrosion of metal. It was interesting to note that in the presence of electral, the LPR value increased and corrosion current decreased. It seems that a protective layer was formed on the metal surface which controlled the rate of corrosion of mild steel in AS, in the presence of electral [11-30].

Mild steel coated with zinc (MS-Zn): When mild steel coated with zinc was immersed in AS, containing electral the corrosion potential was shifted to the cathodic side (when compared with the behaviour of mild steel in AS) (Fig.2a). The cathodic Tafel slope ($b_c$) value was higher than that of the anodic Tafel slope value. This indicates that the change of current with the change of potential was high in the cathodic region than in the anodic region. This is due to the formation of a protective fill on the anodic sites of the metal surface. This prevents the corrosion of metal. It was interesting to note that in the presence of electral, the LPR value decreased and corrosion current increased (from $9.976 \times 10^{-7}$ to $2.359 \times 10^{-6}$ A/cm$^2$). That is, in the presence of electral, the corrosion resistance of mild steel coated with zinc decreased.

SS 316L: In the presence of electral, the corrosion resistance of SS 316L in artificial saliva decreased. This was revealed by the decrease in LPR value (from $5.518 \times 10^6$ to $2.966 \times 10^6$ ohm cm$^2$) and increase in corrosion current (from $8.55 \times 10^{-9}$ to $1.656 \times 10^{-8}$ cm$^2$). The corrosion potential was shifted from -385 to -312 mV vs SCE. The values of Tafel slopes were $b_a = 182$ mV/decade and $b_c=239$ mV/decade. That is, the rate of change of current in the cathodic region was less when compared with that in the anodic region. It is interesting to note that in the presence of electral, the LPR value decreased (from $4.34 \times 10^4$ to $1.902 \times 10^4$ ohms cm$^2$) and the corrosion current increased (from $9.976 \times 10^{-7}$ to $2.359 \times 10^{-6}$ A/cm$^2$). That is, in the presence of electral, the corrosion resistance of SS 316L decreased.

Thus polarization study has led to the conclusion that in the presence of electral, the corrosion resistance of

- Mild steel in artificial saliva increased.
- Mild steel coated with zinc in artificial saliva decreased.
- SS 316L in artificial saliva slightly decreased.

AC impedance spectra

AC impedance parameters such as charge transfer resistance ($R_t$), double layer capacitance ($C_{dl}$) (derived from Nyquist plots) and impedance value log ($Z$/ohm) (derived from Bode plots), of various metals immersed in artificial saliva and artificial saliva containing electral are given in Table 4. The AC impedance spectra are shown in Figures 4 to 6 (Nyquist plots) and Figures 7 to 9 (Bode plots).
Table 3: Corrosion parameters of metals immersed in artificial saliva (SA) in the absence and presence of electrality, obtained by polarization study

<table>
<thead>
<tr>
<th>Metal System</th>
<th>$E_{corr}$, mV vs SCE</th>
<th>$b_1$, mV/decade</th>
<th>$b_2$, mV/decade</th>
<th>LPR, ohm cm$^2$</th>
<th>$i_{corr}$, A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS AS</td>
<td>-657</td>
<td>278</td>
<td>142</td>
<td>2.057 x 10^4</td>
<td>1.983 x 10^6</td>
</tr>
<tr>
<td>MS + Electral</td>
<td>-761</td>
<td>199</td>
<td>167</td>
<td>1.025 x 10^5</td>
<td>3.843 x 10^7</td>
</tr>
<tr>
<td>MS-Zn AS</td>
<td>-855</td>
<td>187</td>
<td>213</td>
<td>4.340 x 10^4</td>
<td>9.976 x 10^7</td>
</tr>
<tr>
<td>MS-Zn + Electral</td>
<td>-915</td>
<td>182</td>
<td>239</td>
<td>1.902 x 10^5</td>
<td>2.359 x 10^6</td>
</tr>
<tr>
<td>SS 316L AS</td>
<td>-385</td>
<td>145</td>
<td>430</td>
<td>5.518 x 10^6</td>
<td>8.551 x 10^9</td>
</tr>
<tr>
<td>SS 316L + Electral</td>
<td>-312</td>
<td>138</td>
<td>626</td>
<td>2.966 x 10^6</td>
<td>1.656 x 10^8</td>
</tr>
</tbody>
</table>

Table 4: Corrosion parameters of metals immersed in artificial saliva (AS) in the absence and presence of electrality obtained from AC impedance spectra

<table>
<thead>
<tr>
<th>Metal System</th>
<th>Nyquist plot</th>
<th>Bode plot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_t$, ohm cm$^2$</td>
<td>$C_{dl}$, F/cm$^2$</td>
</tr>
<tr>
<td>MS AS</td>
<td>779</td>
<td>6.54 x 10^{-9}</td>
</tr>
<tr>
<td>MS + Electral</td>
<td>847</td>
<td>6.023 x 10^{-9}</td>
</tr>
<tr>
<td>MS-Zn AS</td>
<td>650</td>
<td>7.84 x 10^{-9}</td>
</tr>
<tr>
<td>MS-Zn + Electral</td>
<td>564</td>
<td>9.045 x 10^{-9}</td>
</tr>
<tr>
<td>SS 316L AS</td>
<td>29577</td>
<td>0.17 x 10^{-9}</td>
</tr>
<tr>
<td>SS 316L + Electral</td>
<td>60090</td>
<td>8.48 x 10^{-11}</td>
</tr>
</tbody>
</table>

**Mild steel (MS)**

When mild steel was immersed in AS, (Figure 4a) the charge transfer resistance was 779 ohm cm$^2$. The double layer capacitance was $6.54 \times 10^{-9}$ F/cm$^2$. The impedance value $\log(z/\text{ohm})$ was 2.92 (Figure 7a). In the presence of electrality, (Fig.4b), $R_t$ value increased and $C_{dl}$ value decreased. There was increase in the value of impedance $\log(z/\text{ohm})$ (Figure 7b). These observations indicated that in the presence of electrality in artificial saliva, the corrosion rate of mild steel was reduced, due to the formation of protective film formed on the metal surface. The protective film, probably, consisted of oxides of iron and iron complexes of the active principles present in electrality.

**Mild steel coated with zinc (MS-Zn)**

When mild steel coated with zinc was immersed in AS, the charge transfer resistance was 650 ohm cm$^2$ (Fig.5a). The double layer capacitance was $7.84 \times 10^{-9}$ F/cm$^2$. The impedance value $\log(z/\text{ohm})$ was 2.82.
mild steel. That is the protective film formed on the metal surface was less stable and easily broken by the ions present in AS.

Similar observation was made when mild steel coated with zinc was immersed in AS containing electral (Figure 5b). The $R_t$ value decreased from 650 to 564 ohm cm²; the $C_{dl}$ value increased from $7.84 \times 10^{-9}$ to $9.045 \times 10^{-9}$ F/cm²; and the impedance value, log($Z$/ohm), decreased from 2.82 to 2.81. This observation suggested that the film formed on mild steel coated with zinc in AS, in the presence of electral was less stable and easily broken by the ions present in AS.

Figure 6. AC impedance spectra (Nyquist plots) of SS 316L immersed in various test solutions: a) AS, b) AS + electral

Figure 7. AC impedance spectra (Bode plots) of MS immersed in various test solutions: a) Artificial Saliva

Figure 8. AC impedance spectra (Phase plots) of MS immersed in various test solutions: a) Artificial Saliva
Figure 7. AC impedance spectra (Bode plots) of MS immersed in various test solutions: b) AS + electral

Figure 8. AC impedance spectra (Bode plots) of MS-Zn immersed in various test solutions: a) Artificial saliva (AS)
Figure 8. AC impedance spectra (Bode plots) of MS-Zn immersed in various test solutions: b) AS + electral

Figure 9. AC impedance spectra (Bode plots) of SS 316L immersed in various test solutions: a) Artificial Saliva
SS 316L

When SS 316L was immersed in AS, the charge transfer resistance was very high, 29577 ohm cm$^2$. The double capacitance was very low, 0.17 x 10$^{-9}$ F/cm$^2$; and the impedance value log($Z$/ohm) was high, 4.72. These observations suggest that the protective film formed on SS 316L was more stable. It was able to withstand the attack of aggressive ions present in AS. SS 316L is a better candidate in artificial saliva, since it is more corrosion resistant, when compared with mild steel and mild steel coated with zinc.

When SS 316L was immersed in AS containing electral the $R_t$ value was 29577 to 60090 ohm cm$^2$; the $C_{dl}$ value decreased from 0.17 x 10$^{-9}$ to 8.48 x 10$^{-11}$ F/cm$^2$; and impedance value increased from 4.72 to 4.993 log($Z$/ohm). These values suggested that in the presence of electral in AS, the corrosion resistance of SS 316L increased.

AC impedance spectra has led to the following conclusions:

**CONCLUSIONS**

The corrosion behaviour of three metals namely, mild steel (MS), mild steel coated with zinc (MS-Zn) and SS 316L have been studied in artificial saliva in the absence and presence of electral. Polarization study has led to the following conclusions.

In the absence of electral, the order of corrosion resistance was:

SS 316L > MS – Zn > Ms

In the presence of electral, the order of corrosion resistance was:

SS 316 L > MS-Zn > MS

- SS 316L was less corrosion resistant in the presence of electral than in its absence.
- MS was more corrosion resistant in the presence of electral than in the absence of electral.
- MS-Zn was more corrosion resistant in the absence of electral than in the presence of electral.

AC impedance spectra has led to the following conclusions:
In the absence of electral, the order of corrosion resistance was:

SS 316L > MS > MS-Zn

In the presence of electral, the order of corrosion resistance was:

SS 316 L > MS > MS-Zn

- SS 316L was more corrosion resistant in the presence of electral than in the absence of electral.
- MS was more corrosion resistant in the presence of electral than in the absence of electral.
- MS-Zn was more corrosion resistant in the absence of electral than in the presence of electral.

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REFERENCES


