**Corrosion behavior of anodic film formed in calcium hydroxide on Ti-6Al-4V alloy**

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**Abstract**

Surface coloring by anodization of various biomedical implants material is used for clinical application. The resulting anodic oxide layer may affect the corrosion behavior, long-term degradation, and surface inertness of the material. This work investigated the effect of anodization on the corrosion behavior of Ti-6Al-4V alloy. Anodization was performed in KOH–Ca(OH)\textsubscript{2} electrolyte for 20 s. The anodic film gave interference colors of yellow, dark blue, and light blue for anodization at 10, 20, and 30 V, respectively. The corrosion potentials measured by open circuit potential and potentiodynamic polarization modes became nobler with increasing formation voltage, indicating an enhancement in corrosion resistance. The bode phase of electrochemical impedance spectroscopy (EIS) spectra revealed that the film developed at 20 V was more compact than that formed at other voltages, which is in line with the observation by the optical microscope. Furthermore, the long-term immersion of 31 days in modified Ringer’s solution showed that the specimen anodized at 20 V remained intact while film detachment occurred in the other specimens. The anodized surface remained inert similar to the bare substrate after the immersion test, as indicated by no new phase formation detected in the XRD pattern of the specimens.

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**Keywords:** Ti-6Al-4V, anodization, corrosion, interference color.

**Introduction**

It is necessary to differentiate biomedical implants made of different materials, for clinical application. An effective way to differentiate the material is by color code. Despite the type of material, color code is also used to distinguish different parts of the implant. The engineering method for metal coloring included vapor deposition, chrome coating, electrodeposition, and anodization [1]. There was a prerequisite consideration for the coating material that it must be non-toxic and compatible with the human body. Among the available methods, anodization is considered a relatively cheap technique for metal coloring. The characteristics of anodic oxide film resulting from anodization are controllable by tailoring the anodization bath and electrical setup [2]. Anodization did not cause mechanical degradation of the base material [3, 4] and was able to coat surface with complex geometry [5].
Anodization commonly results in a barrier inner layer and a porous outer layer [2]. The barrier layer is thin and compact as opposed to the porous outer layer. For Ti and its alloy, various color is generated by anodization in acid electrolyte such as chromic acid, sulfuric acid, and phosphoric acid [6–9]. Anodization of Ti alloy in phosphoric acid gave a variation of color, including gray, brown, blue, yellow, pink, violet, teal, and green, depending on the applied voltage [10]. The resulting color is attributed to the interference of lights. The anodic film is able to reflect, refract, and absorb incident light. Depending on the thickness and pore characteristics [11], the anodized specimens give a variation of color. Previous results have shown that increasing the formation voltage increased the film thickness and porosity, reducing the refractive index [12].

Surface coloring by anodization can also be done in an alkaline electrolyte such as KOH and NaOH. The alkaline electrolyte is more friendly to the environment and for waste treatment. A similar variation of color as acid anodization can be obtained by alkaline anodization, as reported earlier [13]. The highest refractive index of 1.457 was achieved by anodization at 5 V, while the lowest one was obtained at 40 V [6]. Most of the studies focused on the number of spectrum colors obtained by varying the anodization parameters. The esthetic coloring by anodization may affect the corrosion resistance in corrosive solutions. This work aimed to investigate the corrosion behavior of Ti-6Al-4V alloy after anodization in a mixed alkaline electrolyte KOH–Ca(OH)₂.

**Experimental Method**

Commercial plate of Ti-6Al-4V with composition shown in Table 1 was used as the substrate. The main alloying elements are 6±0.5 wt% Al and 4±0.5 wt% V. The plate having a thickness of 2 mm was cut to give a dimension of 2 × 1 cm². The backside of the specimen was connected to a wire with carbon tape and then molded in an epoxy resin. The specimen was then ground using #800, #1200 and #3000 abrasive papers. Afterwards, the specimen was washed in deionized (DI) water before further use.

<table>
<thead>
<tr>
<th>Table 1. Substrate composition of Ti-6Al-4V alloy.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>wt%</td>
</tr>
</tbody>
</table>

Anodization was performed at a constant voltage of 10, 20, and 30 V using DC power supply (PS-305D) for 20 s. The electrolyte for anodization was mixed of 1 g/l Ca(OH)₂ and 56 g/l KOH solution. For comparison purpose, some specimens were anodized in 56 g/l KOH. The presence of Ca(OH)₂ caused the KOH electrolyte became cloudy. Therefore, the concentration of Ca(OH)₂ was limited to 1 g/l. Cylindrical platinum (Pt) mesh was used as a cathode. The specimen was placed at the center of Pt cylinder. The voltage and current data were recorded using digital multimeter (Rigol DM3068). The electrolyte was maintained at temperature 25±1°C and stirred with magnetic stirrer at 300 rpm during anodization.
The oxide thickness was calculated based on the visible surface color using the corresponding wavelength and refractive index, following Equation 1.

\[ t = \frac{\lambda}{4n_0} \]  \hspace{1cm} (1)

\( \lambda_{\text{max}} \) is the wavelength of maximum absorption (nm), and \( n_0 \) is the refractive index of the oxide. The refractive index for TiO\(_2\) anatase, which is 2.448 [6], is used for the calculation.

The phase composition of the anodic film was detected by X-ray diffractometer (Panalytical X’Pert Pro MPD) using Cu K\( \alpha \) source at 2\( \theta \) range of 30–80\(^\circ\). The XRD pattern was analyzed using highscore software. The mechanical hardness of the anodized specimen was measured using Vickers microhardness (HV3) method using Stuers Durascan 10 series 622. The testing method was performed following ASTM [14].

The degradation behavior was studied using electrochemical corrosion test using CorrTest CS310 potentiostat in 0.9 wt% NaCl solution at 37°C. The specimen was set as the anode, platinum (Pt) as the cathode, and Ag/AgCl in saturated KCl as the reference electrode. Open Circuit Potential (OCP) was measured for 300 s. The EIS test was conducted at frequency range of \( 10^{-1} \)–\( 10^5 \) Hz at potential range of \( \pm 10 \) mV from OCP. Potentiodynamic polarization test was carried out at scan rate of 0.5 mV/s. The result was analyzed using Tafel plot for determining the corrosion potential and corrosion current density.

The apatite forming ability of the anodic film was tested in modified Ringer’s solution. The commercial Ringer’s solution does not contain phosphate ions. Hence, 0.14 g/l Na\(_2\)HPO\(_4\) was added into the solution as the source of phosphate for the formation of Ca–P compound. The composition of the modified Ringer’s solution is listed in Table 2. The specimen was soaked in a hanging configuration in 100 ml of the solution having a pH of 7.4 in a glass bottle. The temperature was kept at 37°C by placing the bottle in a temperature regulated water bath. The presence of apatite was investigated by analyzing the specimen after 31 days immersion with XRD.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reagents</th>
<th>Weight, g in 100 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C(_3)H(_5)NaO(_3)</td>
<td>0.31</td>
</tr>
<tr>
<td>2</td>
<td>NaCl</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>KCl</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>CaCl(_2) \cdot)H(_2)O</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>Na(_2)HPO(_4)</td>
<td>0.14</td>
</tr>
<tr>
<td>6</td>
<td>Ca(OH)(_2)</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Results and Discussion

1. Anodic film formation

The kinetic growth of the anodic oxide layer on Ti-6Al-4V alloy was studied by analyzing the current–time curve. Figure 1 shows the graph of the current density output as a function of time during the anodization, and the surface appearance after the anodization. The curves show a similar trend of a high current density at the initial time and then dropping within 2 s. The curves are typical of anodization curves for the formation of porous anodic oxide film reported elsewhere [3]. The current density generated at the start of anodization is higher at a higher applied voltage, as can be seen clearly in the inset graph, indicating a higher oxidation reaction rate of the metal surface. Ti was oxidized immediately once the voltage was turned on, releasing Ti ions. The saturated Ti ions were then precipitated on the metal surface, forming a barrier oxide film. The barrier layer is a thin but compact layer developed at an early anodization time [15]. The film retarded further metal surface oxidation to a significant degree, as demonstrated by the following a considerable drop of current density. Afterward, the current density was relatively constant at 1 mA/cm² until the end of anodization time. The steady-state current density was related to the growth of porous film on top of the barrier layer [3]. The anodic film gave surface coloration due to optical effects, which involve interference, reflectance, and absorption of lights. Light interference from the direct reflection of incident light at the outermost oxide film and the reflected light at the metal-oxide interface produced a specific wavelength of lights. The thickness and pore characteristics of the oxide film determined the resulting color. Investigation on pore characteristics, including size, geometry, and size, is outside the scope of this research. The surface color depends on the formation voltage: yellow at 10 V, dark blue at 20 V, and light blue at 30 V. The resulting colors were similar to those obtained in pure KOH electrolyte [16]. The results inferred no significant change in the optical properties of the film grown in the Ca-containing electrolyte compared to the Ca-free electrolyte.

![Figure 1](image-url)
Figure 2 shows the plane-view optical microscope images showing the interface of the anodic film and the substrate. The substrate pattern with random black spots and polishing lines remained visible under the film, particularly that formed at 10 V, indicating transparent film. At the higher formation voltage, the thicker film was developed since the substrate morphology was no longer visible through the film. The film developed at 20 V appeared to be more compact than the film formed at 10 and 30 V. The visible color resulted from interference lights from lights reflected by the outer layer and those by the underlying metal substrate. In the visible spectrum, yellow, dark blue, and light blue corresponded to the maximum absorption intensity wavelength of 341.5 nm, 370 nm, and 421 nm [6]. The calculated thickness based on the absorption intensity wavelength and refractive index using Equation 1 is 40, 44, and 50 nm for the oxide formed at 10, 20, and 30 V, respectively. The film became thicker, which is in line with the increase of initial current density in the I-t curve with increasing voltage in Figure 1. Previous work has reported [10, 16] similar results that the oxide film became thicker with increasing applied voltage owing to the increase of oxidation rate.

![Figure 2](image)

Figure 2. Optical microscope image showing the morphology of thin anodic layer as a function of formation voltage.

The elemental composition of the anodized specimens was analyzed by EDS analysis. Figure 3 revealed the elemental concentration of EDS point analysis on the substrate and specimens anodized at 30 V. As expected, the oxygen concentration was significantly high (39–48 at%) and Ti concentration was lower (35–36 at%) in the anodized specimens, confirming the presence of oxide layer, as compared to the substrate. The signal counts for most elements in the substrate decreased due to surface coverage by the oxide layer. The fact that the Al concentration consistently decreased from 10 to 7 at% after anodization in both electrolytes indicated that the oxide layer mainly consisted of titanium oxide. Both K and Ca were not detected by EDS. The K and Ca existed as cations (positively charged ions) in the electrolyte. During anodization, the specimen was set as a positive electrode attracting mainly the anions in the electrolyte. Therefore, there was no significant difference between the composition of oxide formed in the KOH electrolyte and the KOH–Ca(OH)$_2$ electrolyte. The results confirmed the visual observation in Figure 1 and the optical microscope images in Figure 2.
Figure 3. SEM plane-view images of substrate and specimens anodized at 30 V in KOH, and in KOH–Ca(OH)₂, and the corresponding EDS analysis.

Figure 4 displays the XRD pattern of the selected specimens, including the substrate, the specimen anodized at 30 V in KOH and KOH–Ca(OH)₂ electrolytes. The substrate showed the peaks for both Ti and TiO₂. The peaks for TiO₂ anatase mostly overlapped with Ti peaks, particularly at 2θ of 39.9°, 63.2°, and 70.6°. The prominent peak for TiO₂ exists at 57.3° in all specimens and 72.0° in the anodized specimens. The latter peak was only detected in the anodized specimens. The XRD results confirmed that the substrate was covered by the air-formed TiO₂ film, which became thicker after anodization. The relative ratio intensity for TiO₂ in the anodized specimens was higher than the substrate. The anodization produced an oxide layer similar to that existed in the substrate. Ca compound was not detected by XRD, indicating no incorporation of Ca in the film, which was in line with the EDS analysis.

Figure 5 displays the effect of anodization on the mechanical hardness of the alloy. The substrate possessed a hardness value of 326 HV. The hardness for specimens anodized in KOH electrolyte ranged from 328 HV to 343 HV while those anodized in KOH–Ca(OH)₂ electrolyte from 380 to 342 HV with formation voltage. However, the variation in hardness
of the anodized specimens relative to the substrate is considered insignificant, which implied that the film developed as a result of anodization had a similar characteristic with the naturally formed oxide. The results also proved that additive Ca(OH)$_2$ in the electrolyte did not have a significant effect on the mechanical hardness of the resulting anodic film. It is an advantage that the surface protection obtained by the anodization did not alter the surface hardness significantly.

**Figure 4.** XRD pattern of anodized specimens at 30 V in KOH and KOH–Ca(OH)$_2$ electrolytes and the substrate.
2. Electrochemical corrosion

The free corrosion potential of the anodized specimen was investigated by analyzing the open circuit potential (OCP). Figure 6 shows the OCP curves as a function of time in 0.9 wt% NaCl solution at 37°C. The substrate showed a potential transient for the first 50 s, then increased and stabilized at $-0.40 \text{ V}_{\text{Ag/AgCl}}$. Previous reports [17, 18] have shown that the potential of Ti-6Al-4V alloy in 0.9 wt% NaCl was within the range of $-0.5$ to $-0.3 \text{ V}_{\text{Ag/AgCl}}$. The anodized specimen showed a more stable OCP than the substrate. The specimen anodized at 10 V showed a constant voltage of $-0.38 \text{ V}_{\text{Ag/AgCl}}$ during the entire measurement period. The potential consistently shifted to the noble direction with increasing formation voltage of anodization. The noblest potential of $-0.20 \text{ V}_{\text{Ag/AgCl}}$ was obtained in the anodized $-30$ V specimen. The consistent increase of OCP with the formation voltage was attributed to the gain thickness of the anodic oxide layer as a result of anodization. Thicker oxide provided a better corrosion barrier for the underlying metal substrate.

![Figure 5](image1.png)

**Figure 5.** Effect of anodization voltage on surface hardness of the anodized specimen.

![Figure 6](image2.png)

**Figure 6.** Open circuit potential in 0.9 wt% NaCl solution of the specimens anodized in KOH–Ca(OH)$_2$. 
The corrosion behavior of the specimens under a dynamic potential in 0.9 wt% NaCl solution at 37°C is presented in Figure 7. The measurement was repeated four times in four replicate specimens. The curve in Figure 7 was developed by taking an average of four replicate curves for each specimen. The corrosion potential and current density data resulting from the Tafel extrapolation analysis of the curves are presented in Table 3. The substrate exhibited the lowest corrosion potential of $-0.40 \text{ V}_\text{Ag/AgCl}$ with a corrosion current density of $3.88 \times 10^{-7} \text{ A/cm}^2$. The corrosion potential and current density of the Ti-6Al-4V alloy were close to that reported earlier [18]. In agreement with the OCP results, the corrosion potentials of the anodized specimens are nobler than that of the substrate. Meanwhile, the corrosion current density of the anodized specimens remained approximately the same order of magnitude as that of the substrate. The potential shifted towards nobler potential gradually with increasing formation voltage up to $-0.19 \text{ V}_\text{Ag/AgCl}$ for anodized $-30 \text{ V}$ specimen. The susceptibility to corrosion decreases as the corrosion potential becomes nobler. The oxide film thickness played a major role in reducing the susceptibility of the specimen to corrosion. Compared with earlier results on polarization curves of specimen anodized in pure KOH electrolyte which exhibited corrosion potential in the range $-0.55$ to $-0.67 \text{ V}_\text{Ag/AgCl}$ [16], the corrosion potential obtained in this work is approximately 200 mV nobler. The results indicated that additive Ca(OH)$_2$ in the electrolyte effectively enhanced the corrosion resistance of the specimens. The ennoblement of corrosion resistance was possibly due to a thicker barrier layer of the oxide film was developed in the Ca(OH)$_2$ containing electrolyte as demonstrated by the higher current density output (Figure 1) with increasing formation voltage. However, the observation required an advanced characterization technique such as a transmission electron microscope which has not been explored in this work.

**Figure 7.** Potentiodynamic polarization curves in 0.9 wt% NaCl solution at 37°C of the specimens anodized in KOH–Ca(OH)$_2$. 

<table>
<thead>
<tr>
<th>Anodized-30 V</th>
<th>Anodized-20 V</th>
<th>Anodized-10 V</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential (V$_{Ag/AgCl}$)</td>
<td>$-0.1$</td>
<td>$-0.2$</td>
<td>$-0.3$</td>
</tr>
<tr>
<td>Current density (mA/cm$^2$)</td>
<td>$10^{-10}$</td>
<td>$10^{-8}$</td>
<td>$10^{-6}$</td>
</tr>
</tbody>
</table>
Table 3. Corrosion potentials and current densities.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$i_{corr}, \text{A/cm}^2$</th>
<th>$E_{corr}, \text{V}_{\text{Ag/AgCl}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>$3.88 \cdot 10^{-7}$</td>
<td>$-0.40$</td>
</tr>
<tr>
<td>Anodized-10 V</td>
<td>$2.13 \cdot 10^{-7}$</td>
<td>$-0.34$</td>
</tr>
<tr>
<td>Anodized-20 V</td>
<td>$3.21 \cdot 10^{-7}$</td>
<td>$-0.26$</td>
</tr>
<tr>
<td>Anodized-30 V</td>
<td>$3.46 \cdot 10^{-7}$</td>
<td>$-0.19$</td>
</tr>
</tbody>
</table>

Figure 8. EIS spectra in 0.9 wt% NaCl solution at 37°C of the specimens anodized in KOH–Ca(OH)$_2$.

The behavior of the anodic film in 0.9 wt% NaCl solution at 37°C was evaluated by EIS measurements. The response of the anodic film to the alternate current at a wide variety of frequencies is plotted into the Nyquist diagram and bode plots of impedance and phase angle, as presented in Figure 8. The measured data are plotted as data points, and the fitted results are plotted as continuous lines. All the curves were fitted following the same electronic circuit presented in Figure 8d. The fitting parameters are listed in Table 4. The Nyquist curves, which consisted of two semicircles, were represented by two parallel $R$–CPE. $R_s$ represents the solution resistance, $R_1$–CPE1 represents the outer layer of anodic film, and $R_2$–CPE2 represents the inner layer. The Nyquist diagram of the anodized specimens in Figure 8a exhibited a similar shape as the substrate. The results indicated that
the anodic film exhibited similar behavior as the naturally formed oxide. Anodization does not change the corrosion mechanism of the substrate but decreases the corrosion activities. The substrate showed a very small Nyquist curve (Figure 8a). The curves of the anodized specimens became higher at a higher formation voltage. Consistently, the bode impedance of anodized specimens showed higher impedance in all frequency ranges than that of the substrate. Both $R_1$ and $R_2$ values for the anodized specimens in Table 4 are higher than the substrate. The surface resistance consistently increased with increasing formation voltage. The peak shift in the bode phase in Figure 8c was attributed to the porous outer layer of the anodic film. The peak for the anodized $-20$ V specimen was higher, and the peak position was closer to the peak for the substrate, indicating a more compact outer layer.

Table 4. EIS fit parameters.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$R_s$, $\Omega \cdot \text{cm}^2$</th>
<th>CPE1</th>
<th>$n_1$</th>
<th>$R_1$, $\Omega \cdot \text{cm}^2$</th>
<th>CPE2</th>
<th>$n_2$</th>
<th>$R_2$, $\Omega \cdot \text{cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>13.01</td>
<td>$6.42 \cdot 10^{-5}$</td>
<td>0.90</td>
<td>3243</td>
<td>$5.63 \cdot 10^{-5}$</td>
<td>0.62</td>
<td>80029</td>
</tr>
<tr>
<td>Anodized-10 V</td>
<td>16.66</td>
<td>$8.11 \cdot 10^{-6}$</td>
<td>0.84</td>
<td>4267</td>
<td>$1.71 \cdot 10^{-5}$</td>
<td>0.70</td>
<td>601320</td>
</tr>
<tr>
<td>Anodized-20 V</td>
<td>21.66</td>
<td>$6.69 \cdot 10^{-6}$</td>
<td>0.93</td>
<td>7997</td>
<td>$1.43 \cdot 10^{-5}$</td>
<td>0.69</td>
<td>742340</td>
</tr>
<tr>
<td>Anodized-30 V</td>
<td>24.82</td>
<td>$3.84 \cdot 10^{-6}$</td>
<td>0.91</td>
<td>8012</td>
<td>$9.73 \cdot 10^{-6}$</td>
<td>0.80</td>
<td>834720</td>
</tr>
</tbody>
</table>

The evaluation of the apatite forming ability of the specimens after soaking in modified Ringer’s solution was performed by analyzing XRD data. The formation of bone mineral apatite was reported [19–21] to enhance the osseointegration of metallic implant to the host bone. Figure 9 shows the XRD pattern and the surface appearance of the specimens after 31 days of immersion in the modified Ringer’s solution. The data for specimen anodized in pure KOH solution at 30 V is included for comparison purposes. The bright contrast appeared in the anodized-10V-Ca (Figure 9b), anodized-30V-Ca (Figure 9d), and anodized-30V (Figure 9e) surfaces was the exposed metal substrate where the anodic film was locally detached. The substrate (Figure 9a) exhibited a dull appearance except at some spots revealing the bright metallic appearance. Meanwhile, the anodized-20V-Ca specimen remained intact. The more compact oxide layer grown at 20 V was proved to be more resistant to dissolution in corrosive solution. The XRD pattern of all the specimens gave only signal for Ti and TiO$_2$ phases. No indication of Ca-P compound or other new phase was detected by the XRD. Ti and its alloys are known to exhibit bioinert properties in physiological solution preventing apatite deposition on their surfaces [17].
Conclusion

The corrosion behavior of biomaterial Ti-6Al-4V alloy after surface coloring by anodization in KOH–Ca(OH)$_2$ electrolyte using a constant voltage of 10, 20, and 30 V was investigated. The alloy susceptibility to corrosion decreased after anodization, as demonstrated by the ennoblement of corrosion potentials in both open circuit potential and polarization tests results. The potentials became more positive as the film became thicker with increasing formation voltage. The film formed at 20 V exhibited a more compact structure, as confirmed by the optical microscope observation and EIS data. The film formed at 20 V was more resistant to corrosion during long-term exposure in modified Ringer’s solution. The anodized specimens exhibited similar bio inertness as the substrate, as confirmed by the XRD data that no new phase was developed after 31 days immersion in modified Ringer’s solution. The results proved no drawback effect of anodization on both corrosion resistance and inertness of Ti alloy.
Acknowledgments

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