Corrosion Behavior of Dental Alloys Coupled with Titanium
Part 2. The Area Ratio Dependence in Five Solutions

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Sixteen alloys and five pure metals were used and the open circuit potentials (OCP) and the coupled potentials with titanium were measured in five kinds of solutions. All alloys and metals showed the maximum OCP in 1.3% lactic acid solution, and the minimum in 0.01% sodium sulfide solution. The coupled potential depended on the area ratio (alloy/titanium). This dependence was different in every solution. From the area ratio dependence of the coupled potential, the potassium fluoride solution was thought to be active with pure titanium. In contrast, sodium sulfide solution was thought to be active with the alloys and the metals. The effect of the co-existence of pure titanium was very small in the sodium sulfide solution.

Key words: Corrosion, Electrochemical property, Titanium

INTRODUCTION

The excellent corrosion resistance of titanium is widely known1-3). With increased dental application of titanium, its electrochemical behavior when co-existing with dissimilar dental alloys has been extensively studied4-9). Some studies measured the area ratio dependence for the couple of carbon7), amalgams8,9) and gallium alloy9) with titanium and its alloy. The coupled potential of some kinds of dental alloys with pure titanium was reported at two meetings10,11) and the area ratio (alloy/titanium) dependence was measured in Ringer's solution in Part 112). A relation between the area ratio and the coupled potential was very clearly shown.

In the present study, four kinds of solutions, 0.9% potassium fluoride, 1% nitric acid, 1.3% lactic acid and 0.01% sodium sulfide, were used in the coupled potential measurement.

The characteristic features of each solution were described previously8,12-32). Among the various electrolytes, sodium chloride solution was used in many studies13-19). Ringer's solution is basically NaCl solution (0.9%NaCl+0.1% chlorides and other chemicals). It was used to examine the aluminum bronze alloys by the galvanostatic and tarnish test20) and in the immersion test of the Ag-Pd-Cu alloy system21). It was also used in Part 1 of this study12).

The oxide film on the surface of pure titanium is attacked by ionizable fluoride compounds, such as NaF and HF22). The effect of the fluoride ion was also discussed in some studies8,23). Johansson et al.8) used 0.9% NaCl solution with and without
fluoride ions to measure the charge transfer between amalgam and titanium. The existence of the fluoride ions increased the amount of charge transfer. Siirilä et al.\textsuperscript{23} immersed titanium test pieces in toothpastes, gel and varnish containing fluoride compounds. If titanium contacted with gel or varnish for a long time, it was corroded by the fluoride ions, but for short periods no immediate deterioration to titanium was observed in the mouth.

For passivation of titanium and its alloys, nitric acid is very effective\textsuperscript{24}. In some studies\textsuperscript{7,25,26}, 30-40\% nitric acid at 50-60\degree C was used for 20-30 min to passivate titanium alloys, Co-Cr alloy and stainless steel. If the same acid was used for one min with acoustic agitation, the procedure became surface-cleaning\textsuperscript{26}.

Nakayama et al.\textsuperscript{21,27} used lactic acid solution for the immersion test of an Ag-Pd-Cu alloy system. Geis-Gerstorfer et al.\textsuperscript{15} used 0.1 M lactic acid +0.1 M sodium chloride solution for immersion and polarization measurement of four Ni-Cr alloys. Patro et al.\textsuperscript{28} used artificial saliva with and without 0.1 M lactic acid for silver alloys. By addition of the lactic acid, weight loss\textsuperscript{15} and corrosion current increase\textsuperscript{28} were observed.

Sodium sulfide solution has been used in both immersion and electrochemical tests\textsuperscript{21,29–32}. The concentration of the solution was 1-2 \%. Pure silver and Ag-Cu eutectics were severely attacked by the sulfur ion in the immersion test\textsuperscript{21}.

Among the solutions used in the present study, 0.9\% potassium fluoride would attack the titanium surface rather than the dental alloys. Although the concentrated nitric acid was used for passivation, it was unclear how 1\% nitric acid solution worked for titanium. The lactic acid and sodium sulfide solutions would be active for silver alloys.

In the present study, the findings in Ringer's solution in Part 1\textsuperscript{12} were added, and the effects of five kinds of solutions were compared. The method in Part 1 was applied to examine the area ratio dependence of the coupled potential in each solution.

MATERIALS AND METHODS

The alloys, the instruments and the basic measuring methods were similar to those reported in Part 1\textsuperscript{12}. For convenience of explanation, the minimum necessary tables and figures are shown again. The alloys and metals used in this experiment are listed in Table 1. Thirteen kinds of commercial alloys, three test binary alloys and five pure metals were used. The test solutions used in this experiment are listed in Table 2.

From each alloy, at least two specimens (16×12 mm\textsuperscript{2}) were cast. A stainless steel wire was welded to the specimen as the lead wire, and it was mounted with epoxy resin. The wire was sealed using a vinyl tube. The specimens were polished with 600-grit SiC paper without water. The surface was cleaned with water and methyl alcohol. After polishing, the specimen was immersed in the test solution. The lead wire was connected to the instruments for potential measurements shown in
Table 1 Alloys and metals used in this experiment

<table>
<thead>
<tr>
<th>Code</th>
<th>Brand name</th>
<th>Composition</th>
<th>others</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Au</td>
<td>Ag</td>
</tr>
<tr>
<td>Gold alloys</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D GC Casting Gold M.C. (Type III)</td>
<td>75</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>E GC Casting Gold M.C. (Type IV)</td>
<td>70</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>F Shofu Super Gold (Type III)</td>
<td>74</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>G Shofu Super Gold (Type IV)</td>
<td>70</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>ST Degussa Stabilor NF IV (Type IV)</td>
<td>55</td>
<td>29</td>
<td>0</td>
</tr>
<tr>
<td>Silver palladium alloys</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O GC Castwell M.C.</td>
<td>12</td>
<td>45</td>
<td>18</td>
</tr>
<tr>
<td>P Ishifuku Kimpalla S-12</td>
<td>12</td>
<td>51</td>
<td>15</td>
</tr>
<tr>
<td>Q GC Microcast M.C.</td>
<td>–</td>
<td>55</td>
<td>18</td>
</tr>
<tr>
<td>N Tokuriki New Pala S-2</td>
<td>–</td>
<td>56</td>
<td>25</td>
</tr>
<tr>
<td>Test alloys</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3 Ag-Pd binary</td>
<td>–</td>
<td>70</td>
<td>–</td>
</tr>
<tr>
<td>P2 Ag-Pd binary</td>
<td>–</td>
<td>80</td>
<td>–</td>
</tr>
<tr>
<td>C2 Ag-Cu binary</td>
<td>–</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Cobalt chromium alloys</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H Sankin Suncolium Hard</td>
<td>57</td>
<td>&gt;23</td>
<td>&gt;5</td>
</tr>
<tr>
<td>Y Shofu Summalloy Titan</td>
<td>40</td>
<td>23</td>
<td>28</td>
</tr>
<tr>
<td>Nickel chromium alloys</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X Hi-Chrom Soft (High Dent. S.)</td>
<td>–</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>S Sankin Suncolium Soft</td>
<td>–</td>
<td>10</td>
<td>85</td>
</tr>
<tr>
<td>Pure metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au pure gold</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag pure silver</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd pure palladium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu pure copper</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ti pure titanium</td>
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</table>

Table 2 Test solutions used in this experiment

1. Ringer's solution
   (NaCl 9.08 g, KCl 0.43 g, CaCl₂ 0.24 g, NaHCO₃ 0.20 g in 1 litter)
2. 0.9% potassium fluoride solution
3. 1% nitric acid solution
4. 1.3% lactic acid solution
5. 0.01% sodium sulfide solution

Fig. 1. The potential was measured using an electrometer (HE-105A, Hokuto Denko, Tokyo, Japan) and recorded by a hybrid recorder (Type 3087, Yokogawa, Tokyo, Japan) at five minute intervals. The room temperature was 24±1 °C, and the solution temperature was 23±1 °C.

Three kinds of potentials were measured.

\( V_A \): the potential of the alloy or pure metal listed in Table 1 (vs. saturated calomel electrode, SCE)
**V_T**: the potential of pure titanium (vs.SCE)

**V_C**: the potential of coupled alloy with titanium (vs.SCE)

The potentials **V_A** and **V_T** were measured simultaneously (Fig. 1a). For the measurement of **V_C**, the lead wires of the alloy and titanium were connected to the same positive terminal of the electrometer. The standard electrode was connected to the negative terminal. The coupled potential was measured for 30-60 min and the potentials **V_A** and **V_T** were measured individually again.

The surface area was changed using nail varnish to obtain area ratios of around 0.1 to 10 (alloy/titanium). To examine whether or not the coupled potential, **V_C**, depends on the area ratio, "deviation from the alloy potential", \((V_A-V_C)/(V_A-V_T)\), was calculated for each area ratio. This value shows the difference between the coupled potential and the alloy potential. A large value means a large effect of the presence of titanium on the coupled potential. For each alloy, at least five points were used to calculate the regression line (the area ratio vs. the potential deviation).

**RESULTS**

*Open circuit potential*

The measurement of the potential of the alloy and pure titanium commenced soon after immersion in the solution. The potential showed time dependence in most of the alloys and metals. Two examples are shown in Fig. 2. The degree of time-dependence was different among the alloys and also among the solutions. In most cases, the potential became almost constant after 60 min. Therefore, 60 min after immersion, the coupled potential was measured for 30 min (40-60 min when it was changing) and then the first measurement (**V_A** and **V_T** individual measurement) was reinstated.
The $V_A$ and $V_T$ values just before the measurement of the coupled potential were averaged and the open circuit potential (OCP) of the alloys and metals in each solution was obtained. The results are plotted in Fig. 3. In all of the alloys and metals, the largest potentials were seen in both nitric and lactic acid solutions. The lowest potentials were seen in the sodium sulfide solution. Especially in pure silver, alloys containing large amounts of silver (P2 and C2), and pure copper, the potential was very low in sodium sulfide solution. In potassium fluoride solution, pure titanium and Co-Cr and Ni-Cr alloys showed low potentials. For Ringer's solution, the same
values reported in Part 1 are shown. Pure titanium showed the smallest potential range between maximum and minimum.

**Schematic coupled potential curve**

After this potential was recorded, the coupled potential was measured. Before the examples are shown, the schematic potential curves are shown and the basic features are explained in Fig. 4.

After immersion in the test solution, the potential $V_A$ and $V_T$ changed as shown by the curves AB and CD. The starting points of the measurements are A and C (1st step). The coupled potential is shown as the curve EG, depending on the area ratio (2nd step). Then each potential was measured again, starting from points G and J (3rd step). Each potential showed a transition period GH and JK. The curves HI and KL were on the extension of the curves AB and CD, respectively, in most cases. Point E was always between B and D. If the area ratio becomes large (the area of the alloy becomes large), point E moves closer to point B. If the area ratio becomes smaller, point E moves closer to point D. This is expressed quantitatively by the value of “deviation from the alloy potential”, $(V_A-V_C)/(V_A-V_T)$, and as BE/BD in Fig. 4. Sometimes the coupled potential curve shows a small dip just like the first part of EF. In such a case, the curves AB and CD are extended to the end of the dip and $B'E'/B'D'$ is used as the potential deviation. The curves EF were obtained for five to ten values of the area ratios in each alloy and each solution.

**Examples of coupled potentials**

Actual examples of the effect of the area ratios are shown in Fig. 5. The potential curves were superimposed coinciding with the end of the OCP curves of each of the alloys and metals (point B in Fig. 4). In Fig. 5, the first and the terminal part of the curves of $V_A$ and $V_T$ were omitted. Only four curves were selected to show the examples. The numbers above or below each coupled potential curve are the area ratio (alloy/titanium). The OCP curves of pure titanium differed with the fluctuation of the potential of both specimens (titanium and the alloy). In the figures, the findings
Fig. 5 Examples of the potential measurement.
(1) alloy E (gold alloy, Type IV)
(2) alloy P (Ag-Pd-Cu-Au alloy)
in Ringer's solution were quoted from Part 1\textsuperscript{2}).

In Fig. 5(1), the example of alloy E is shown. With a decrease in the area ratio (with a decrease in the area of the alloy), the curves of the coupled potential became closer to the pure titanium curve. All of the potential curves were stable.

In the third step, the potential curves of both specimens returned to form extensions of the original curves in a short time. In Fig. 5(2), the curves of the alloy P (Ag-Pd-Cu-Au alloy) were very unstable in the sodium sulfide solution, but were very stable in the other four solutions.

**Deviation from the alloy potential**

From these figures, "deviation from the alloy potential", $BE/BD$ or $B'G'/B'D'$ in Fig. 4, was calculated for each coupled potential curve in each solution. Thus, the plotting of the area ratio vs. potential deviation from the alloy (%) was obtained in Fig. 6 for alloy F (gold alloy, Type III) in each solution. The vertical axis expresses the deviation of the coupled potential from the alloy potential. A value of 100% means that the coupled potential was equal to the potential of pure titanium. The value of zero area ratio means that only pure titanium exists. Therefore, for the value of zero area ratio, the potential deviation should be 100%. The potential deviation changed very quickly when the area ratio was below 2.0. The difference among the solutions was not clear from this figure. Plotting the area ratio ($r$) vs. the logarithm potential deviation ($\log d$) appeared to be linear. Semi-logarithm plotting was also tried. The regression equation is given by:

$$\log d = b_0 - b_1 \cdot r.$$  \hspace{1cm} (1)

The indexes $b_0$ and $b_1$ were decided by the least-squares method. In this calculation, the point (0,100) was included. An example of the plotting and the estimated

![Fig. 6 Plotting of area ratio vs. deviation from alloy potential (%).](image)

![Fig. 7 Plotting and regression lines (alloy F: gold alloy).](image)
regression lines for alloy F are shown in Fig. 7. With increasing area ratio, the potential deviation from the alloy decreased. This means that the coupled potential becomes close to the alloy potential with increasing area of the alloy. When the influence of titanium is strong, the deviation would still be large even if the area of the alloy becomes large. This was expressed in this figure as a small gradient line. In contrast, a steep slope implies a weak influence of titanium. The slopes of the regression lines differed greatly among the solutions. In this case, the contact with titanium was effective in the potassium fluoride and nitric acid solutions, and less effective in the lactic acid and sodium sulfide solutions.

Regression lines
For all of the alloys and metals in all of the solutions, the same regression lines were calculated using equation (1). The results are shown in Figs. 8 and 9. The result for Ringer’s solution (Fig. 8(1)) is the same figure shown in Part 1. All of the measured coupled potentials for one alloy were used for the calculation of equation (1). Therefore, all of the data of one alloy in one solution were concentrated in one regression line in Fig. 8.

In all of the solutions, pure gold, gold alloys and silver alloys showed similar tendencies. Pure metals and the binary alloys showed different slopes in Ringer’s solution. The slopes of Co-Cr and Ni-Cr alloys were scattered in nitric and lactic acid solutions.

The alloy O (Ag-Cu-Pd-Au alloy) showed lower intercepts in nitric and lactic acid solutions. The alloy C2 (Ag-Cu eutectic) also showed low intercepts in Ringer’s and sodium sulfide solutions. In Figs. 8(3)-(5), the expression “deviation zero” appears for Ag, Cu and C2. This indicates that the coupled potential is always the same as the potential of the alloy or metal even if titanium co-exists.

Pure palladium and the alloys P2 and P3 (Ag-Pd alloys) showed similar tendencies as pure gold and gold alloys. Only in sodium sulfide solution did they show a small intercept.

Another expression of the results is shown in Fig. 9 for some alloys and pure metals. The shallow slope for the potassium fluoride solution and the steep slope for the sodium sulfide solution are clearly shown in this figure.

DISCUSSION
Selection of the electrolytes
In this study, five kinds of solutions were used. The negative ion in Ringer’s solution is chloride. Except for the sodium sulfide solution, the concentration of negative ions was the same in each case of full dissociation. To obtain the same molarity of negative ions in the sodium sulfide solution, the necessary weight % of Na₂S was about 1.3%. In immersion and polarization tests, 2 to 0.1% Na₂S concentrations were used, but in the present study the concentration was reduced to 0.01% to obtain the stable potential-time curves and coupled potential curves. The five kinds of
(1) Ringer's solution

Area ratio

Deviation from alloy potential (%)

Au alloys & Ag alloys

(2) Potassium fluoride solution

Area ratio

Deviation from alloy potential (%)

Au alloys & Ag alloys

(3) Nitric acid solution

Area ratio

Deviation from alloy potential (%)

Au alloys & Ag alloys

Co-Cr and Ni-Cr alloys

pure metals and binary alloys

Co-Cr and Ni-Cr alloys
solutions and their concentrations in Table 2 were thus decided.

Open circuit potentials
In Fig. 3, the average open circuit potential is shown for each alloy and metal in each solution. Pure silver and pure copper showed especially low potentials in sodium sulfide solution. Silver combines with sulfur and forms black sulfide very easily. If palladium is present at more than 25% in silver, the corrosion is negligible for clinical use. The test alloy P3 (Ag-30%Pd) showed a similar potential as the commercial Ag-based alloys (O,P,Q and N), but the potential of P2 (Ag-20%Pd) was lower. The amount of 20%Pd was not sufficient for sulfur attack. The other test alloy C2
Fig. 9 Regression lines: comparison of the effect of the solutions. (1) alloys (2) pure metals.

(Ag-20%Cu) was a typical eutectic, but its potential was higher than either pure silver or pure copper, and comparable with P2. This phenomenon will be discussed later.

In the potassium fluoride solution, pure titanium showed the lowest potential among the alloys and metals. The Co-Cr and Ni-Cr alloys also showed low potentials. The concentration of the fluoride ion was very low, but it had some effect on the surfaces of titanium, Co-Cr and Ni-Cr alloys.

Examples of coupled potential
The effect of the area ratio on the coupled potential is shown in Fig. 5 for two alloys. The potential curves of titanium in the first step were sometimes scattered widely. This was caused by the fluctuation of the potentials of both titanium and the coupled alloy at the time when the coupled potential measurement was started. The length of the first step was not constant (60 to 90 min), because the time necessary to obtain an almost constant potential differed among the alloys. Therefore, the final part, which is shown in Fig. 5 shows the fluctuation. These fluctuations appeared to have no negative effect on the plotting in Figs. 6-9. Therefore, the measurement and the calculation of the potential deviation were continued.

In the third step, the potential curve sometimes did not return to the extension of the curve in the first step. This point was briefly discussed in presentations of the two meetings. The details will be discussed when the reactions of the solutions with the alloys have been measured more precisely.
Deviation from the alloy potential
In Figs. 8 and 9, the difference among the solutions is clearly shown.

Potassium fluoride solution: The slopes of the regression lines are very shallow. The effect of titanium was strong in this solution. Johansson et al. observed an increase of the current between titanium and amalgam in fluoride containing saline solution. They suggested that this was caused by the reduction of oxide film by fluoride addition. In this experiment, the oxide film may be formed during the measurement of the open circuit potential. The surface of titanium was attacked by the fluoride ion, and may have become active. This could be the reason why the slope of the regression lines were shallow in this solution. The alloy C2 (Ag-Cu eutectic) shows an exceptionally steep slope. This reason will be described elsewhere.

Sodium sulfide solution: In contrast, all alloys and pure metals showed the steeper slopes. The difference in the slopes among the alloys was small. It may be that the alloys and the metals reacted actively with the sulfur ion rather than titanium. In Fig. 3, the open circuit potential was very low in the sodium sulfide solution for all alloys and metals. This also shows the activity of this solution for all of the alloys and the metals.

Ringer's solution: Pure metals and the binary metals showed steeper slopes than those of other alloys. The intercept of the alloy C2 (Ag-Cu eutectic) was very small and was out of the r-log d relation. In the immersion test in this solution, pure Ag and the alloy C2 markedly decreased the reflectance and its color changed to black. This extremely strong reaction with the solution is the reason for being out of the r-log d relation.

Nitric acid solution: The effect of this solution on the titanium surface appeared to be weak. In Fig. 3, Ti shows a similar open circuit potential as those of other alloys. In Fig. 8(3), Ag and Cu shows zero deviation. These metals are active for nitric acid solution. The slopes of Co-Cr and Ni-Cr alloys are very scattered. The reason is the very small difference in the potentials between titanium and the alloys (VA - VT). The smaller intercepts of the alloys D(gold alloy) and O(Ag based alloy) cannot be discussed based on the findings of the present experiment alone.

Lactic acid solution: Pure copper and the alloy C2 showed zero deviation. In the immersion test, pure silver and the alloy C2 showed no color change, but alloy C2 showed weight loss in this solution. The weight loss indicates an active reaction with the solution. The reason for the scattered slopes of Co-Cr and Ni-Cr alloys is the same as the case of the nitric acid solution.

The importance of the area ratio and the selection of the electrolytes has become clear in this study. Similar future studies will be enhanced by the potentiodynamic polarization technique and microstructure observation.

CONCLUSIONS
Thirteen kinds of commercial dental alloys, three test alloys and five pure metals were used and the open circuit potential and the coupled potential with pure titanium
were measured in five kinds of solutions.
1. All of the alloys and metals showed a maximum open circuit potential (OCP) in 1% nitric acid solution and minimum in 0.01% sodium sulfide solution.
2. In most of the couples, the potential of the polished titanium was lower than that of the coupled alloy or metal.
3. The difference between the alloy potential and the coupled potential decreased with increasing area ratio (alloy/titanium).
4. The area ratio and the logarithm of this potential difference (normalized by the potential difference between the alloy and titanium) showed a linear relationship in most of the alloys and metals.
5. From this linear relationship (regression lines), the difference among the solutions was clearly shown.
6. The potassium fluoride solution was thought to be active at the titanium surface. Pure titanium gives a great contribution to the coupled potential.
7. The sodium sulfide solution reacted with the alloys and metals rather than pure titanium. The effect of the co-existence of pure titanium was minimal.

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