Corrosion Behavior of Dental Alloys in Various Types of Electrolyzed Water

Hongwei DONG1,2, Yuki NAGAMATSU2, Ker-Kong CHEN3, Kiyoshi TAJIMA2, Hiroshi KAKIGAWA3, Sizhen SHI1 and Yoshio KOZONO2

1Pedodontics Research Institute, Tongji University, 2, Lane 158, DaMuQiao Rd., Ste. 402 Shanghai, 200032, P.R. China 2Department of Materials Science 3Department of Operative Dentistry, Kyushu Dental College, 2-6-1 Manazuru, Kokurakita, Kitakyushu, 803-8580 Japan

Received July 14, 2003/Accepted October 3, 2003

The corrosion behavior of dental alloys was examined in electrolyzed strong acid water, weak acid water and neutral water using a 7-day immersion test. The precious metal alloys, gold alloy, Au-Ag-Pd alloy and silver alloy showed the greatest surface color change and dissolution of constituents in the strong acid water and the smallest in the neutral water. The release of Au from gold alloy was especially marked in the strong acid water. Co-Cr alloy showed greater corrosion and tarnish resistance in the strong acid water rather than in the weak acid water and the neutral water. X-ray microanalysis revealed that the corrosion products on the precious metal alloys were silver chloride crystals and the thin brown products on Co-Cr alloy were cobalt and chromium oxides. Ti was sound in all three types of electrolyzed water. The neutral water appeared the least corrosive to metals among the three types showing equivalent bactericidal activity.

Key words: Electrolyzed water, Dental alloys, Corrosion

INTRODUCTION

Electrolyzed water has attracted great attention because of its excellent bactericidal and virucidal activities and its less undesirable effects on biological tissues and the environment1-3). Its application has been investigated in operative, prosthodontic and other fields in dentistry4-14). The electrolyzed water available in the market is roughly classified into three categories: strong acid water, weak acid water and neutral water according to their pH values. Strong acid water was first introduced and has been the most widely utilized in dentistry. We previously reported its effectiveness in the sterilization of impressions, instruments and denture8-14), in which the experimentally bacteria-contaminated surfaces were thoroughly cleaned with a 1-minute ultrasonic washing in this water while a 20-minute washing could do little to remove the bacteria in distilled water. Also, this treatment caused neither deformation nor surface roughness on the impression and gypsum casts as seen in sterilization with chemical solutions10). However, there are two major concerns with this water: one is the deterioration of its bactericidal activity during storage, and the other its
tendency to corrode metals. Although the three types of electrolyzed water are different from each other in pH, oxidation-reduction potential (ORP) and residual chlorine, they all have the same excellent bactericidal effects8-14). Comparative studies revealed that the bactericidal effect of the strong acid water disappeared one week after preparation, the neutral water kept its effect for three months and the weak acid water for a slightly shorter period13).

The electrolyzed water is used for many medical and dental remedial treatments. The authors have been surveying the acceptability of these waters for gargling in order to minimize the risk of infection before treatment or keep the affected part clean after treatment. It is one of the requirements for this purpose that the water be less potentially corrosive to metal restorations. Yoshida15,16) and Nomasa et al.12) separately demonstrated characteristic corrosion of metallic products in strong and weak acid water. In the present study, corrosion behaviors of dental alloys in strong acid, weak acid and neutral water were examined. Changes in surface appearance and corrosion products of the alloys immersed in the waters were observed and the released constituent elements from the alloys were analyzed.

MATERIALS AND METHODS

Specimens of dental alloys
The dental alloys used are listed in Table 1. The specimens were prepared by casting according to each manufacturer’s directions to form plates sized 1.5×1.5×0.1 cm. The castings were sand-blasted, polished with SiC abrasive papers and finally finished with #1000 SiC abrasive paper. They were ultrasonically cleaned in acetone prior to the immersion test.

Immersion test in electrolyzed waters
The three types of electrolyzed water used are shown in Table 2 with their properties at 23±2°C. The strong acid water (SW), weak acid water (WW) and neutral water (NW) were prepared by electrolyzing a 0.05% sodium chloride aqueous solution, tap water altered by specified electrolysis and tap water containing 5% sodium chloride,

<table>
<thead>
<tr>
<th>Table 1 Dental alloys used</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloys</strong></td>
</tr>
<tr>
<td>Gold alloy¹</td>
</tr>
<tr>
<td>Au-Ag-Pd alloy²</td>
</tr>
<tr>
<td>Silver alloy³</td>
</tr>
<tr>
<td>Co-Cr alloy⁴</td>
</tr>
<tr>
<td>Ti⁵</td>
</tr>
</tbody>
</table>

¹Casting gold type III, Ishifuku Metal Industry Co. Ltd., Tokyo, Japan
²New gold-palladium, Ishifuku Metal Industry Co. Ltd., Tokyo, Japan
³SILVER II, Ishifuku Metal Industry Co. Ltd., Tokyo, Japan
⁴COBALTAN, Shofu Inc., Kyoto, Japan
⁵Pure Titanium A, J Morita MFG Corp, Kyoto, Japan
Table 2 Electrolyzed waters used

<table>
<thead>
<tr>
<th>Electrolyzed water</th>
<th>Code</th>
<th>pH</th>
<th>ORP (mV)</th>
<th>Residual chlorine (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong acid water</td>
<td>SW¹</td>
<td>2.3</td>
<td>1,121</td>
<td>75.3</td>
</tr>
<tr>
<td>Weak acid water</td>
<td>WW²</td>
<td>6.9</td>
<td>825</td>
<td>50.3</td>
</tr>
<tr>
<td>Neutral water</td>
<td>NW³</td>
<td>7.1</td>
<td>581</td>
<td>37.7</td>
</tr>
<tr>
<td>Tap Water</td>
<td>TW</td>
<td>7.3</td>
<td>476</td>
<td>0.9</td>
</tr>
</tbody>
</table>

¹SUPER WATER mini, Hirata Corp., Osaka Japan
²ACIDENT, J. Morita Tokyo MFG. Corp., Tokyo Japan
³AP aqua21, Asahipretec Corp., Kobe, Japan

respectively, each with exclusive apparatus. Tap water (TW) was also used for comparison.

The specimens were suspended with a nylon lines tied to small protrudes made by grinding the sprue parts and immersed in 40 ml of testing water in capped bottles made from polystyrene 3.65 cm in diameter and 7.42 cm in height at 37°C for 1, 2, 3, 4, 5 and 6 hours, and 1, 3, 5 and 7 days. The characteristic properties of the water type at 37°C could be regarded within the ranges 23±2°C shown in Table 2 from the previous report¹⁴). At each immersion time, the used water was preserved for analysis of the released elements from the alloy. The specimen was immersed again in the fresh water until the next scheduled time.

The used water was analyzed based on the calibration curve method with an atomic absorption spectrophotometer (Z-9000, Hitachi Ltd.) to detect the amount of the released elements from the alloy.

All the experiments were performed for three specimens and the results were statistically analyzed by one-way ANOVA and Scheffe's t-test.

Observation and analysis of corrosion products

The change in the surface appearance of each specimen after immersion in water was observed using macroscopic photography for 7 days. The surface of the 7-day specimen was observed using a scanning electron microscope (S-4300 FE-SEM, Hitachi Ltd.) and analyzed with an energy dispersive X-ray microanalyzer (EMAX-550, Hitachi Ltd.) to define the corrosion products.

RESULTS

Change in surface appearance

Fig. 1 shows the change in surface appearances of dental alloys during the 7-day immersion in each type of electrolyzed water. In SW, the surface of the gold alloy lost its luster and a whitish film was formed during the 3-hr immersion. The film became thicker as the immersion time increased. No changes in appearance were observed for the 7-day immersion in WW, NW and TW (Fig. 1a).

The surface of Au-Ag-Pd alloy appeared gray at 3 hours and gradually turned black as the immersion time increased in SW. WW caused the surface changes on
Fig. 1 Surface color change of dental alloys in electrolyzed waters.
Fig. 2 Dissolution of gold alloy in electrolyzed waters.

Fig. 3 Dissolution of Au-Ag-Pd alloy in electrolyzed waters.

the alloy to a lesser extent, and changes in NW even less (Fig. 1b).

In the silver alloy, the surface of the specimen became a brown or black color after 3-hr immersion in all types of water. The changes were the most severe in SW and the least in NW. A slight change in appearance was observed for the 7-day specimen in TW (Fig. 1c).
Co-Cr alloy showed quite a different corrosion behavior from the precious metal alloys. No color changes were found in SW during the 7-day testing period. The surface appearance became a yellowish brown in WW and NW. The changes were more marked in WW than in NW (Fig. 1d).

No changes in appearance were recognized for Ti in any water throughout the 7-
Release of constituent elements

The cumulative amounts of the constituent elements released from the dental alloys by immersion in the three types of electrolyzed waters for 7 days are shown in Figs. 2 to 5. For the gold alloy, the most notable dissolution was found in SW (Fig. 2). The cumulative amount of released elements for the 7-day period was predominantly the largest for Au, followed in decreasing order by Cu, Pt, Pd and Ag \((p<0.01)\). In WW, the release of Au was significantly smaller than in SW. The other elements were also released less and the total amount of the released elements was significantly smaller than that of SW \((p<0.01)\). The dissolution of the gold alloy further decreased in NW.

For Au-Ag-Pd alloy, Cu was markedly released in SW \((p<0.01)\), while the other elements such as Ag and Zn showed a smaller release (Fig. 3). No Au and Pd were detected from this alloy. The release of Cu was markedly decreased in WW, and more so in NW. However, the total amount of the released elements from this alloy was significantly larger than that of the gold alloy in WW and NW \((p<0.01)\).

For the silver alloy, the release of In was predominant in SW \((p<0.01)\) (Fig. 4). The alloy released only a small amount of Ag and Zn although their amounts were significantly larger than those in WW and NW \((p<0.05)\). No release of In was detected in WW and NW.

The Co-Cr alloy showed quite a different behavior from the precious alloys (Fig. 5). The largest release of the elements was caused in WW. Both Co and Cr were almost equally released and the amounts increased with immersion time. The dissolution of the alloy significantly decreased in NW and the amount was approximately half that of WW. In SW, only a small amount of Co was detected.

No release from Ti was detected in SW, WW and NW for the 7-day period.

All the alloys showed no measurable release of their constituents in TW.

Corrosion products

Figs. 6 and 7 show the SEM images and spectra of X-ray microanalysis of the surface of the specimens after 7-day immersion in SW and WW, respectively. Granular corrosion products were observed all over the surface of the gold alloy immersed in SW. They were found to be rich in Ag and Cl by spot microanalysis. Similar results were obtained for Au-Ag-Pd alloy and silver alloy in SW. When the specimen was immersed in WW, the corrosion products insularly distributed on the surface of Au-Ag-Pd alloy while the surface of silver alloy was almost fully covered by corrosion products. Although the individual crystals composing the corrosion layer appeared somewhat rectangular, they showed the same spectra as those in SW. There were scattered corrosion products on the Co-Cr alloy immersed in WW, among which Co, Cr and O were detected.
DISCUSSION

Among the various types of electrolyzed water, the strong acid water is the most acidic and it has been feared that metals might be corroded if they were treated with it. In fact, some reports demonstrated the severe corrosion of metals immersed in
In the present study, the precious metal alloys showed the largest amount of dissolution of their constituent elements in SW. It is notable that the total dissolution was the largest for the gold alloy. Especially, Au was predominantly released from the gold alloy, Cu from the Au-Ag-Pd alloy and In from the silver alloy, while only a little dissolution of Ag was detected. One of the authors previously reported...
that In was also much released from In containing amalgam in a 0.5% sodium chloride solution\textsuperscript{17}. It is generally known that Au shows no dissolution in strong acid other than aqua regia. It was also reported that gold alloy has a good corrosion resistance in sodium chloride solution\textsuperscript{18}. On the other hand, it was demonstrated that the dissolution of Au was accelerated in an acid medium containing chloride\textsuperscript{19}. It is known that the strong acid water contains a larger fraction of Cl\textsubscript{2} in its residual chlorine\textsuperscript{20}. And Yoshida\textsuperscript{15} has reported that gold alloy greatly corroded in strong acid water. Thus, the corrosion behavior of gold in SW in the present study might be attributed to the interaction of the lower pH and higher concentration of residual chlorine. The dissolution of the gold alloy significantly decreased in WW and further decreased in NW. The total dissolution similarly decreased in WW and NW for the Au-Ag-Pd alloy and silver alloy. The manufacturer of NW claims that most of the residual chlorine consists of hypochlorous acid (HClO) and it is not easily converted into gas due to the specified double electrolyzing process. Thus NW contains less free chlorine than other types of electrolyzed water. This may be the reason why NW was less corrosive to metals together with its neutrality.

The surface of the gold alloy lost its luster after the 3-hr immersion in SW and turned whitish in appearance as immersion time increased. No changes in appearance were observed in WW and NW during the 7-day immersion period. In the Au-Ag-Pd alloy, the surface turned black during the 3-hr immersion in SW and got darker as immersion time increased. The surface changes were less in WW and the least in NW. In the silver alloy, all the specimens suffered from severe color changes after the 3-hr immersion in all types of water. SEM observation and X-ray microanalysis of the 7-day specimens revealed that the surface was covered with granular corrosion products consisting of Ag and Cl rich layers on all the precious metal alloys when immersed in SW. These products might be identified as the crystals of AgCl. It may be supported by findings that AgCl crystals were generated on the surface of Au-Ag-Pd alloy in 1% NaCl, as well as in the human saliva and artificial saliva\textsuperscript{21} and on the surface of silver alloy in Ringer's solution and 0.1%N HCl solution\textsuperscript{22} during anode polarization measurements. Although in the SEM images the crystals appeared somewhat rectangular when the specimen was immersed in WW or NW, they were identified as equally AgCl by X-ray microanalysis. Furthermore, the surface appearance was variously changed from whitish to black colors according to the alloy, water and immersion time. However, X-ray microanalysis showed that all the corrosion products were AgCl crystals and the present experiment could not systematically explain the differences in the apparent color of the corroded surface. In any case, it was found from these results that Ag in the precious metal alloys might not easily dissolve into electrolyzed water, but preferentially react with residual chlorine in the waters to form AgCl crystals on the surface.

Unlike the precious metal alloys the Co-Cr alloy showed the least corrosion in SW. Its surface remained unchanged during the 7-day immersion. This might be due to the passivation in the water. It was rather corroded in WW, exhibiting the largest amounts of released Co and Cr and its surface turned yellowish brown with the
corrosion products of Co and Cr oxides after 3-hr immersion. Similar tendencies were observed in NW but those levels were significantly lower than in WW.

Ti specimens showed superior corrosion resistance in all the types of electrolyzed water, being quite sound in any water throughout the 7-day immersion test.

Little measurable corrosion behavior was found in tap water during the 7-day period in the dental alloys used except for silver alloy which showed a slight change in surface appearance after 7-day immersion.

Electrolyzed water has been used in dentistry not only for sterilization of dental materials and instruments to avoid secondary infection but also for various therapeutic treatments. It has been confirmed from experiments and clinical experiences that all the three types of water employed in the present study are commonly effective for these treatments. They each have little risk of undesired side effects, irritation to biological tissues or contamination of the environments. It is therefore expected that their uses will further increase in the place of chemicals. Gargling with them will be effective for disinfection before dental treatments and for maintenance of post-treatments. However, the risk of metal corrosion is one of the important factors preventing their application for that use. Provided that patients gargle for one minute with it for three times a day, the immersion for seven days in this experiment corresponds to the actual exposure of the alloy to the water for more than 9 years. It may not mean therefore that the precious metal alloy restorations will rapidly react with SW to release large amounts of Au, Cu or In in the practical use. However, the use of SW for daily gargling should be avoided from the biological point of view. In addition, acid waters may not always be acceptable to patients because they have somewhat unpleasant chloric smell and have the potential to corrode metallic restorations. On the contrary, it is suggested that NW will be the most acceptable among the types because it is almost tasteless and odorless and less corrosive to metals as found in the present study. Furthermore, it was demonstrated that NW showed excellent hemostatic activity over the conventional hemostatic agents, and its further clinical application is expected.

REFERENCES


