The effect of oxidizing water on metallic restorations in the mouth:  
*In vitro* reduction behavior of oxidizing water

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Abstract: Mouth-rinsing with oxidized water which contains electrolytically generated chlorine is known to hinder dental plaque formation and growth, but it also accelerates the deterioration of metallic restorations in the mouth. The present work consists of an *in vitro* study to elucidate the electrochemical reactions involved in the reduction of oxidized water on dental alloys through a systematic investigation of the potentiostatic polarization behavior of dental alloy electrodes. The five dental alloys selected for investigation were gold alloy, gold alloy containing platinum, silver-palladium-gold alloy, conventional amalgam and high copper amalgam. The corrosion potentials of all dental alloy electrodes were shown to be more noble in oxidized water than in 0.1N sodium chloride solution. The potential differences between the corrosion potentials were relatively small in the case of amalgam electrodes. The polarization curves for all of the dental alloy electrodes in oxidized water revealed reduction currents of chlorine, hypochlorous acid, dissolved oxygen and oxonium ion. The reduction of chlorine and hypochlorous acid started at a more noble potential than that of dissolved oxygen. The dental alloys studied, except the amalgams, did not dissolve excessively at the corrosion potentials in oxidized water.

Key words: oxidized water; dental alloy; corrosion; polarization curves.

Introduction

Devices that can safely and simply produce chlorinated water through electrolysis of low concentration saline have recently been placed on the market[1-2]. The chlorinated water produced with these devices is referred to by different names according to the manufacturer[3], and manufacturers generally emphasize the oxidizing power of this water in choosing a name. In this paper, the chlorinated water produced using such devices will be referred to as oxidizing water, since this water (solution) has oxidizing potential[3].

The use of oxidizing water to sterilize a variety of objects has been assessed, and it has begun to be used clinically and in other settings[4-9]. Because chlorinated water does not appear to be toxic[10], its use in the oral cavity has been proposed[5,11]. In a study previously conducted by the author and his coworkers from the viewpoint of periodontology[12], human dentin pieces retained mechanically in the oral cavity were washed either with oxidizing water or physiological saline twice a day (in the morning and the evening). In that study, we found that less plaque formed on the dentin pieces washed with oxidizing water than on the pieces washed with physiological saline. Based on this finding, we suggested that oxidizing water might be useful as a plaque-suppressing gargle, however, a number of questions need to be answered before oxidizing water is widely used for that purpose[13]. One question pertains to the possibility of decalcification of hard tooth tissue when exposed to strongly acidic oxidizing water whose pH level is about 3 or less (equal to the pH of HCl). Our previous experiment *in vitro* demonstrated that hard tooth tissue is unaffected by brief gargling with this water[13]. However, the results of an experiment by other investigators in which metallic material used in the oral cavity was immersed in oxidizing water, suggested that oxidizing water could accelerate corrosion of such material[14]. In connection with this finding, it has been effective chlorine concentration required for chlorinated water to function as a disinfectant is not very high and that chlorinated water loses its oxidizing power soon after it has oxidized organic substances such as protein[6,11,15]. However, when we previously examined the electric potentials of metallic restorative material before and after gargling with oxidizing water, the potential shifted to the noble range after gargling and the metallic restorative material was oxidized by oxidizing water[9].

To examine the effects of oxidizing water in oxidizing restorative metals in greater detail, we examined the reduction profiles of dental metals exposed to oxidizing water *in vitro*. The reason for conducting this study *in vitro* was that the experimental conditions could be kept constant.

It is well known that corrosion of a metal involves both oxidation of the metal and reduction of the oxidizing agent, i.e., oxidizing agents become reduced as they oxidize metals. Since these reactions take place at a solid-liquid interface, the rate of reduction of the oxidizing agent is determined by the surface state and the oxidation potential of the metal. Therefore, the present study was aimed at examining reduction profiles (i.e., oxidizing power) of a given metal at a wide range of
electric potentials, rather than measuring the extent of oxidation of individual restorative metals with different histories. Furthermore, since previous studies demonstrated that chloride ions accelerate the corrosion of dental metals\textsuperscript{[16-22]}, we also tested NaCl-supplemented oxidizing water.

### Materials and Methods

#### 1. Electrodes

Sample electrodes made of a gold alloy (20K), a platinum-supplemented gold alloy (PtAu), a gold-silver-palladium alloy (PdAg), and two different amalgams (CP and DJ) were prepared, as shown in Table 1. The electrodes made of gold alloy, platinum-supplemented gold, and gold-silver-palladium alloy were prepared according to the method reported by Kikuchi\textsuperscript{[18]}. Amalgam electrodes were prepared by the method of Kobayashi\textsuperscript{[16]}. Immediately before use, the sample electrodes were polished with water-resistant polishing paper No. 1200 (Sankyo), while applying water to the electrode throughout the polishing process. A platinum electrode served as the counter-electrode. A saturated calomel electrode (HC-205, Toa Denpa Kogyo) was used as the reference electrode. Potentials relative to the reference electrode are expressed in V (SCE) units in this paper. Potentials relative to the reference electrode are expressed in V (SCE) units in this paper.

#### 2. Solutions

The following solutions were tested: (1) oxidizing water, (2) oxidizing water diluted in a ratio of 1:2 (dilute oxidizing water), (3) oxidizing water supplemented with NaCl to a final concentration of 0.1N (0.1N NaCl-supplemented oxidizing water), (4) dilute oxidizing water supplemented with NaCl to a final concentration of 0.1N NaCl-supplemented dilute oxidizing water, and (5) 0.1N NaCl solution. The oxidizing water was prepared with a Sedent Pyrenizer (SD1000, Sekimura). The pH of the oxidizing water was 2.9±0.1. The oxidation-reduction potential of the oxidizing water determined using the voltmeter attached to the Sedent Pyrenizer was 1100 mV or higher (relative to the 3.3M silver chloride electrode). The Sedent Pyrenizer is capable of producing 40 liters of oxidizing water at a time using stock solution prepared by dissolving 120g NaCl in 0.8 liters of water.

Each test solution was used at room temperature without being deoxidized. A 100 ml hard-glass beaker was used as an electrolysis cell, and 50-ml volumes of each solution were tested. An electromagnetic stirrer (M-21, Yamato Kagaku) fitted with a 3 cm Teflon-coated agitator was used to agitate the test solutions.

#### 3. Apparatus for potential scanning

A potential scanner (HB-101, Hokuto Denko) was attached to a potentiostat (HA-502, Hokuto Denko) to obtain polarization curves, which were recorded with an X-Y recorder (F-35, Riken Denshi).

#### 4. Test procedure

1) Non-agitated solutions

The sample electrode was polished and washed in water. It was then immersed in oxidizing water or dilute oxidized water. Cathode and anode scans between the corrosion potential and −1.3V (SCE) were started immediately at a rate of 10 mV/s to obtain polarization curves. The scanning range for the NaCl solution was between the corrosion potential of a given sample electrode in oxidizing water and −1.3V (SCE). With the amalgam electrodes, scanning was first performed for a range between the corrosion potential in each solution and −1.3V (SCE), and the range was then expanded to include 0.0V (SCE) or the potential level at which the oxidation current was about 3 mA/cm².

The solutions tested without agitation were oxidizing water, dilute oxidized water, and 0.1N NaCl.

2) Agitated solutions

The sample electrode was polished and washed in water. It was then immersed in a test solution and the solution was agitated. Cathode scans were then conducted at a rate of 10 mV/s for a range between the corrosion potential and −1.3V (SCE). Polarization curves were thus obtained.

Solutions tested with agitation were oxidized water, dilute oxidized water, 0.1N NaCl-supplemented oxidizing water, 0.1N NaCl-supplemented dilute oxidizing water, and 0.1N NaCl.

### Results

#### 1. 20K electrode

Figures 1 and 2 show the results for the 20K electrode. No characteristic oxidation-reduction currents were recorded when this electrode was immersed in non-agitated oxidizing water (OXW) or non-agitated dilute oxidizing water (1/2 OXW) (Fig. 1). In agitated solutions, the reduction current for this electrode increased markedly, and the current was greater in oxidizing water than in dilute oxidizing water throughout the range of potentials tested. In non-agitated 0.1N NaCl (Fig. 2), the oxidation current was greater than in oxidizing water (Fig. 1) when anode scans were conducted at potentials over 0.0V (SCE). In agitated 0.1N NaCl, the reduction current was greater than in non-agitated 0.1N NaCl when scans were performed at potentials lower (more base) than −0.2V (SCE). The reduction current in agitated 0.1N NaCl remained almost unchanged at 1 mA/cm² when scans were conducted between −0.6 and −1.1V (SCE). The results in 0.1N NaCl-supplemented oxidizing water and 0.1N NaCl-supplemented dilute oxidizing water (Fig. 2) were similar to those in NaCl-free oxidizing water and dilute oxidizing water, respectively (Fig. 1).
2. PtAu electrode

Figures 3 and 4 show the results for the PtAu electrode. In non-agitated oxidizing water and dilute oxidizing water, no characteristic oxidation-reduction currents were seen (Fig. 3). In agitated solutions, the reduction currents increased markedly. Thus the profiles of this electrode in oxidizing water and dilute oxidizing water were similar to those of the 20K electrode (Fig. 1). Its profiles in NaCl solution and 0.1N NaCl-supplemented oxidizing water (Fig. 4) also resembled those of the 20K electrode (Fig. 2).

3. PdAg electrode

Figures 5 and 6 show the results for the PdAg electrode. In non-agitated oxidizing water and dilute oxidizing water, the reduction currents were low, but a peak reduction current was recorded at a potential of about 0.0V (SCE) (Fig. 5). In agitated solutions, the reduction currents increased markedly. The reduction current in oxidizing water was greater than in dilute oxidizing water throughout the range of potentials scanned. In oxidizing water, the reduction current had a low peak between 0.0 and -0.2V (SCE). In non-agitated 0.1N NaCl solution (Fig. 6), no characteristic oxidation-reduction currents were seen. In agitated 0.1N NaCl solution, the reduction current at potentials lower (more base) than -0.2V (SCE) was greater than in non-agitated 0.1N NaCl solution. The reduction current in agitated 0.1N NaCl solution remained almost unchanged at 1 mA/cm² throughout the potential range between -0.6 and -1.1V (SCE). The results in agitated 0.1N NaCl-supplemented oxidizing water and agitated 0.1N NaCl-supplemented dilute oxidizing water (Fig. 6) were similar to those in agitated NaCl-free oxidized water and dilute oxidized water (Fig. 5), respectively, except for the appearance of clear reduction current peaks at 0.1 and -0.1V (SCE) in the former solutions.
4. CP electrode

Figures 7 and 8 show the results for the CP electrode. In non-agitated oxidizing water, high oxidation currents were recorded at potential levels higher (more noble) than -0.6V (SCE). Relatively high reduction currents were also yielded by cathode scans (Fig. 7). The polarization curves in dilute oxidizing water were similar to those in oxidizing water, but the currents were lower in dilute oxidizing water throughout the potential range scanned. Agitation of oxidizing water and dilute oxidizing water resulted in higher reduction currents. Throughout the potential range scanned, the reduction current was higher in agitated oxidizing water than in agitated dilute oxidizing water. In non-agitated 0.1N NaCl solution (Fig. 8), high oxidation currents were recorded at about -0.4V (SCE). Reduction currents at potentials lower (more base) than -0.9V (SCE) were greater in agitated 0.1N NaCl than in non-agitated 0.1N NaCl. The reduction current in agitated 0.1N NaCl tended to become constant when the potential reached -1.1V (SCE). The results in agitated 0.1N NaCl-supplemented oxidizing water and 0.1N-NaCl-supplemented dilute oxidizing water (Fig. 8) were similar to those in agitated NaCl-free oxidizing water and dilute oxidizing water (Fig. 7), respectively, except that reduction currents began to be noted at a potential level of about -0.4V (SCE) in the former solutions.

5. DJ electrode

Figures 9 and 10 show the results for the DJ electrode. In non-agitated oxidizing water, currents changed slightly depending on the potential levels, but they were relatively low (Fig. 9). Agitation of oxidizing water and dilute oxidizing water resulted in higher reduction currents. Throughout the potential range scanned, the reduction current was higher in agitated oxidizing water than in
agitated dilute oxidizing water. In non-agitated 0.1N NaCl solution (Fig. 10), only small currents were recorded at any potential levels. The reduction current for a potential range lower (more base) than −1.0V (SCE) was greater in agitated 0.1N NaCl than in non-agitated 0.1N NaCl. In agitated 0.1N NaCl, the reduction current tended to become constant when the potential reached about −1.1V (SCE). In agitated 0.1N NaCl-supplemented oxidizing water and 0.1N NaCl-supplemented dilute oxidizing water (Fig. 10), reduction currents began to be noted at about 0.0 to −0.1V (SCE). The results in these two solutions were similar to those in NaCl-free oxidizing water and dilute oxidizing water (Fig. 10), except that a peak reduction current was recorded at about −0.6V (SCE) in the NaCl-supplemented solutions.

Discussion

1. Test metals and their oxidation profiles

In the present study, a gold alloy, a platinum-supplemented gold alloy, a gold-silver-palladium alloy and two different amalgams were selected as test metals. These alloys had been used for tooth restoration in the subjects of our previous study examining changes in oral cavity potentials following gargling with oxidizing water[3]. In that study[3], the degree of oxidation of the restorative metals was estimated on the basis of actually measured potentials in the oral cavity and the polarization curves reported by Yamaoka[17]. The validity of our estimation in that study was corroborated by the results of the present study, because oxidation currents for a given range of potentials were small for test metals immersed in non-agitated 0.1N NaCl, oxidizing water, and dilute oxidizing water. Next, the oxidation profiles of metals in non-agitated solutions will be presented in detail.

1) Gold alloy and platinum-supplemented gold alloy

When the 20K electrode (Figs. 1 and 2) and PtAu electrode (Figs. 3 and 4) were immersed in NaCl solution or oxidizing water, no marked oxidation currents were visible for a range of potentials up to about 0.8V (SCE), suggesting that these alloys are unlikely to become corroded in the presence of noble potentials if exposure to such potential is brief. In the study conducted by Yamaoka[17], oxidation currents were examined for a range of potentials up to 0.2V (SCE). The present study clearly showed that these alloys do not undergo intense oxidation even when exposed to potentials higher (more noble) than 0.2V (SCE).

When the 20K electrode was immersed in NaCl solution (Fig. 2), relatively high oxidation currents were recorded by anode scans in a range of potentials higher (more noble) than 0.0V (SCE). This probably reflects oxidation of the copper contained in the alloy. Cathode scans for the same range of potentials revealed almost no oxidation currents, allowing us to conclude that the 20K electrode immersed in the NaCl solution undergoes only transient oxidation, not undergo long-lasting oxidation. The potential of metallic restorative material in the oral cavity tends to gradually increase (become more noble) as the frequency of gargling with oxidizing water increases[3]. Such a slow increase in potentials seems to be attributable to the transient oxidation observed in the present study.

The polarization curves for the gold alloy and the platinum-supplemented gold alloy showed no peak currents associated with the formation and reduction of silver chloride[18, 19]. This means that the state of the alloy surface did not allow the silver in the alloy to react with chlorine. If silver chloride had been produced in the oral cavity, it is unlikely that the potential would have risen above 0.1V (SCE) (become more noble). In practice, however, the potential is about 0.2V (SCE) under such circumstances[3]. Thus, the surface of the gold alloy tested in the present study was close to that of the gold alloy inserted into the oral cavity for tooth restoration.
2) Gold-silver-palladium alloy

When the PdAg electrode (Figs. 5 and 6) was immersed in NaCl solution and oxidizing water, no marked oxidation currents were visible for a range of potentials up to about 0.4V (SCE), results similar to those obtained with the gold alloy. Accordingly, severe corrosion of the PdAg electrode is unlikely to occur in NaCl solution even when exposed to noble potentials for brief periods.

When the same electrode was immersed in non-agitated oxidizing water or dilute oxidizing water, peak currents associated with the reduction of silver chloride were especially high when the corrosion potential is small. The peak currents associated with the reduction of silver chloride were seen at a potential of about 0.0V (SCE), even when exposed to noble potentials for brief periods.

3) Amalgam

When the conventional amalgam (CP electrode; Figs. 7 and 8) was immersed in NaCl solution and oxidizing water, high oxidation currents were seen at potentials lower than 0.0V (SCE). When a high-copper amalgam (DJ electrode; Figs. 9 and 10) was immersed in oxidized water, high oxidation currents were seen at potentials lower than 0.0V (SCE). When a high-copper amalgam without superficial oxidized layers and in the conventional amalgam at a potential level of about 0.0V (SCE) in agitated oxidizing water (Fig. 9), the peak reduction current for oxidized copper was seen at about 0.5V (SCE), indicating slight oxidation of copper in this solution.

We previously reported that amalgams inserted into the oral cavity undergo small changes in potential following gargling with oxidized water, because amalgams are more likely to be oxidized than other metals. Once a superficial oxidized layer is formed on amalgams, as on the DJ electrode used in this study, they are unlikely to be oxidized even immediately after polishing. It is also known that amalgams lose their surface tin when long periods have elapsed after their insertion into the oral cavity. Bearing all this in mind, the degree of oxidation of amalgams can be said to be much lower than usually expected of a fresh restorative material without an oxidized surface layer.

2. Reduction profiles of oxidizing water

The substances contained in oxidizing water that can be reduced, i.e., the substances which can act as oxidizing agents, include dissolved oxygen, chlorine and hydrogen ions, and the dissolved oxygen is known to often act as an oxidizing agent in corrosive reactions of dental metals. A number of studies have been conducted concerning the reduction profiles of dissolved oxygen associated with dental metals. Measurement conditions in the present study were determined on the basis of these past studies. When the reduction profiles of the plane of metals with poorly oxidized layers are studied, the electrode is first thoroughly reduced at base potentials, and anode scans are then performed. Cathode scans were performed beginning at the corrosion potential level in the present study for the following reasons: (1) if reduction is conducted at base potentials, the solution in the vicinity of the electrode becomes alkaline and dissociation of hypochlorous acid takes place there, making the experimental conditions more complex; and (2) we wanted to study reduction profiles on the electrode surfaces in the presence of corrosion potentials. The reduction of dissolved oxygen, chlorine, and hydrogen ions will be separately discussed below.

1) Reduction of dissolved oxygen

Since dissolved oxygen is the only oxidizing agent contained in NaCl solution, agitated 0.1N NaCl solution will be discussed here.

When the 20K electrode (Fig. 2), the PtAu electrode (Fig. 4), the PdAg electrode (Fig. 6) and the DJ electrode (Fig. 10) were immersed in agitated 0.1N NaCl solution, reduction currents (about 1 mA/cm²), independent of po-
tential levels, were recorded. These reduction currents are associated with dissolved oxygen and are involved in the following diffuse controlled reaction.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (1) \]

These currents are independent of potentials and electrode material\[30-37\]. The current for the CP electrode was about 2 mA/cm² (Fig. 8). This is because the oxides formed at corrosion potentials are also reduced simultaneously. If the reduction current in non-agitated solution is deduced from this current, the result is equal to the current for the other electrodes.

The dissolved oxygen reduction waves for the 20K and PtAu electrodes differed from the wave for the PdAg electrode. As the potential increased from about -0.2V (SCE), the reduction current did not show a smooth increase with the 20K and PtAu electrodes. With the PtAu electrode (Fig. 4), a rather clear biphasic wave was visible. This indicates that when the potential was close to -0.2V (SCE), the four-electron reaction shown above did not take place, and reduction discontinued prematurely during the formation of hydrogen peroxide.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2\text{O}_2 \quad (2) \]

When the polarization curves of Yamaoka\[17\] were analyzed, non-smooth negative polarization curves were obtained for the platinum-supplemented gold alloy alone. This is probably because reduction of dissolved water takes place via the two reactions described above. Prior to the present study, no investigations had ever reported measuring dissolved oxygen reduction currents for dental gold alloys immersed in agitated solutions. However, the potential levels and waveforms for pure gold\[38\], reported to date, were similar to those obtained in the present study for gold alloys.

Moreover, with the PdAg electrode (Fig. 6), dissolved oxygen reduction currents began to increase at a potential level of about -0.2V (SCE), and the increase was smooth. Yamaoka also reported smooth negative polarization curves\[17\]. This means that hydrogen peroxide formation is negligible at this setting.

With the amalgams (CP electrode, Fig. 8; DJ electrode, Fig. 10), dissolved oxygen reduction currents began to increase at a potential level of about -0.9V or -1.0V (SCE), consistent with previous reports\[30,34,36,39\]. When anode scans are started on the base side of the high copper amalgam, where no oxidized layer has been formed, hydrogen peroxide formation via the reaction (2) is seen at potential levels between -0.5 and -1.0V (SCE). In the present study, this reaction could not be precisely measured because cathode scans were started on the noble side. However, the data yielded by cathode scans also suggest that small amounts of hydrogen peroxide were formed. That is, the reduction current began to increase at a potential of about -0.5V (SCE) when the DJ electrode was immersed in agitated solutions.

2) Chlorine reduction

Oxidizing water is chlorinated water produced by electrolysis. When dissolved in water, gaseous chlorine molecules are hydrolyzed as follows:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \quad (3) \]

As a result, the chlorinated water becomes acidic, and hypochlorous acid is produced. Hypochlorous acid dissociates as follows:

\[ \text{HClO} \rightarrow \text{H}^+ + \text{ClO}^- \quad (4) \]

Here, the acid dissociation constant is 5.6 x 10⁻⁸\[40\]. This dissociation is therefore negligible when the pH is in the acidic range.

Chlorinated water or chlorine-dissolved seawater is industrially used to prevent microbial attachment to cooling facilities. For this reason, the possibility of corrosion by chlorine or hypochlorous acid has also been studied\[41-43\]. Ives et al. studied this issue by analyzing reduction curves obtained by immersing pure gold electrodes in chlorinated water at different pH levels\[38\]. The potential and waveform of the reduction curves for our PtAu electrode in agitated NaCl-supplemented oxidizing water (Fig. 4) conformed closely to those reported by Ives et al.\[39\]. Therefore, the following discussion is based on their views.

Taking agitated NaCl-supplemented oxidized water (Fig. 4) as a typical example, the reduction current began to increase at a potential of 0.76V, corresponding to the corrosion potential, and increased further at potentials of 0.4V and -0.2V. Thus, the reduction current increased in three steps. According to Ives et al.\[39\], chlorine molecules are reduced when the potential is most noble (0.76V (SCE)).

\[ \text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- \quad (5) \]

Next, hypochlorous acid is reduced.

\[ \text{HClO} + \text{H}^+ + 2e^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad (6) \]

When the potential is most base (-0.2V (SCE)), hypochlorous acid ions are reduced.

\[ \text{ClO}^- + 2\text{H}^+ + 2e^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad (7) \]

However, considering that reduction of hypochlorous acid ions also occurs in basic solutions, the following formula is also possible.

\[ \text{ClO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^- \quad (8) \]

In the present study, the waveform for the 20K electrode in oxidizing water supplemented oxidizing water (Figs. 1 and 2) was basically the same as for the PtAu electrode in the same solutions (Figs. 3 and 4). This indicates that chloride is reduced in similar stages. For both the 20K and PtAu electrodes, the reduction current at the most noble potential level was higher in NaCl-supplemented oxidizing water than in NaCl-free oxidizing water. This reflects to the fact that the addition of chloride ions causes a leftward shift of the equilibrium of Formula 3 and elevates the concentration of chlorine molecules.

In agitated oxidizing water, reduction waves began to be seen at a potential level of about 0.4V (SCE). The reduction current at a potential of about 0.0V (SCE) in oxidizing water was about double that in dilute oxidized water. Thus, the above-mentioned reduction mechanism seems to be valid when explaining the reactions which take place prior to the reduction of hypochlorous acid.

Reduction of hypochlorous acid, which takes place at a potential of about -0.2V (SCE), seems to involve another mechanism, which will be discussed below.

As shown in Figs. 2 and 4, the increase in the reduc-
tion current in dilute oxidizing water beginning at a potential of about −0.2V (SCE), conforms well with the increase in the dissolved oxygen reduction current. It is therefore reasonable to consider that the increase in reduction currents for this range of potentials reflects reduction of dissolved oxygen. The increase in reduction currents associated with the reduction of hypochlorous acid was smaller than in the dissolved oxygen reduction current. This is because hydrogen peroxide reduces the chlorine or hypochlorous acid in the vicinity of the electrode. In the potential range at which the dissolved oxygen reduction current is about 1 mA/cm², the formation of hydrogen peroxide ceases, and the reduction currents show an increase comparable to that seen at a potential level of about 0.0V (SCE). Thus, at this experimental setting, the reduction of hypochlorous acid can be said to continue until the potential reaches about −1.2V (SCE). Since the hydroxide ions formed by reaction (1) cause dissociation of hypochlorous acid, it can also be concluded that hypochlorous acid ions cause reduction of dissolved oxygen on the electrode surface.

With both the 20K and PtAu electrodes, the reduction current at base potentials was abnormally high in oxidizing water, when compared with the values in dilute oxidizing water. This will be discussed in the section on hydrogen-ion reduction.

No chlorine molecule reduction currents were seen with the PdAg electrode, and hypochlorous acid reduction currents began to be noted at a potential of about 0.4V (Figs. 5 and 6). The hypochlorous acid reduction current overlaps the reduction currents of silver chloride and other oxides formed at corrosion potentials levels, however, the reduction profiles of this electrode are basically the same as those of the gold alloy electrode. Because dissolved oxygen reduction is unaccompanied by hydrogen peroxide formation with the PdAg electrode, relatively high reduction currents of hypochlorous acid were recorded even at potential levels at which dissolved oxygen began to be reduced.

With the CP electrode, the reduction current pattern in agitated NaCl-supplemented oxidizing water (Fig. 8) was equivalent to the dissolved oxygen reduction pattern in NaCl solution, although it shifted towards the noble range (about −0.4V). This probably represents overlapping of hypochlorous acid reduction currents with the reduction currents of the many oxides reduced simultaneously in this potential range in oxidizing water, as shown in the results in non-agitated oxidizing water (Fig. 7).

With the DJ electrode (Figs. 9 and 10), hypochlorous acid reduction currents began to be seen at a potential level of 0.0V (SCE). In the potential range more base than the reduction current peak for copper oxides,[18-20] the reduction wave was equivalent to the dissolved oxygen reduction wave, although it shifted towards the noble range (about −0.6V). A copper oxide reduction current peak was seen in agitated oxidizing water, but not in non-agitated oxidizing water. These results with the DJ electrode probably represent overlapping of hypochlorous acid reduction currents with the reduction currents of the oxides formed in large amounts, the same as with the CP electrode.

3) Hydrogen-ion reduction

Hydrogen-ion reduction profiles have been studied for amalgams,[44-47] silver alloys,[48] and pure silver, copper, etc.[49], and the results of these studies suggest that hydrogen ion reductive reactions are not involved in corrosion of dental metals even in acidic solutions.[47,49] However, no such studies have been conducted with gold alloys or gold-silver-palladium alloys.

Ives et al.[38] measured hydrogen-ion reduction currents with pure gold electrodes and found that when the electrodes were immersed in 0.6N NaCl (pH 3.2), hydrogen-ion reduction currents began to be noted at a potential of about −0.7V (SCE). When a 20K electrode was immersed in agitated NaCl-supplemented oxidized water in the present study (Fig. 2), the polarization curve had a turning point at about −0.8V (SCE), although this point was not very clear. This indicates that hydrogen ions began to be reduced at this potential level and reached a limiting current level when the potential was about −1.0V (SCE). No such turning point was observed with the PtAu electrode (Fig. 4), but a reduction current similar to that for the 20K electrode was seen, and a limiting current was also noted. These findings suggest that hydrogen ions are reduced with the PtAu electrode, the same as with the 20K electrode. When these two electrodes were immersed in oxidizing water free of chloride ions, none of them showed limiting currents (Figs. 1 and 3). This is probably because reduction of hydrogen ions started at lower base potential levels in the absence of acceleration of hydrogen-ion reduction by chloride ions.

As shown in Figs. 2 and 4, the increase in reduction currents due to the addition of currents associated with reduction of dissolved oxygen was small in dilute oxidizing water, and no signs of hydrogen-ion reduction were detected in this solution. This is probably because the hydroxide ions formed by reduction of dissolved oxygen neutralized the hydrogen ions near the electrode at the hydrogen-ion concentration prevailing in this dilute (1:2) oxidizing water.

No clear turning point was seen in the polarization curve with the PdAg electrode either (Figs. 5 and 6). This suggests that hydrogen ions were reduced following an increase in the currents associated with the reduction of dissolved oxygen. It is known that with pure silver, hydrogen ions begin to be reduced at a potential of about −0.65V (SCE)[49], and the PdAg electrode seems to resemble pure silver. The changes in the waveform depending on whether chloride ions were present were also similar with the PdAg electrode and the gold alloy electrode. With the PdAg electrode, the reduction current in dilute (1:2) oxidizing water was high, and no neutralization of hydrogen ions by reduction of dissolved oxygen was observed. It seems that more silver chloride may be reduced with the PdAg electrode than the gold alloy electrode or that hypochlorous acid has a buffering effect on the PdAg electrode alone. However, it is still impossible to draw any definite conclusions.
With amalgams, hydrogen reduction from hydrogen ions becomes marked at a potential of about -1.0 to -1.2V (SCE), and hydrogen formation from water molecule begins at a potential of about -1.8V (SCE). When the CP electrode (Fig. 7) and the DJ electrode (Figs. 9 and 10) were immersed in oxidizing water or NaCl-supplemented oxidizing water, reduction currents increased sharply at a potential level of -1.0V (SCE), probably reflecting reduction of hydrogen ions. In dilute (1:2) oxidizing water, the increase in reduction currents was small, because reduction of dissolved oxygen occurred in this potential range, resulting in neutralization of hydrogen ions.

3. Oxidizing water and oxidation of test metals

When the gold alloy, platinum-supplemented gold alloy, and gold-silver-palladium alloy were immersed in oxidizing water, the potential was more noble than the potential previously measured in the oral cavity following gargling with oxidizing water (Figs. 1 through 6) [3], but no marked oxidation currents were recorded in this potential range. Therefore, it seems unlikely that these alloys undergo severe corrosion following short-time gargling.

Based on a report concerning potentials in the oral cavity [3], hypochlorous acid seems to act as the major oxidizing agent of metallic restorative material exposed to oxidizing water. Hydrogen ions and dissolved oxygen do not seem to be directly involved in the oxidation of these metals because they react with these metals only at very base potential levels. Hypochlorous acid was also found to act as a major oxidizing agent in the case of the amalgams. Thus, the pH of oxidizing water does not directly accelerate the corrosion of metallic restorative material, but it can affect corrosion indirectly through its effects on the stability of oxides and dissociation of hypochlorous acid.

According to a published study [3], no marked change in potential in amalgam was seen following gargling with oxidizing water. This is because potentials are unlikely to change with amalgams that are susceptible to oxidation, as shown by our study of the CP electrode. However, as discussed in Section 2-3), the degree of oxidation of amalgam after insertion into the oral cavity should be much lower than expected from the results of the present study, when we consider that the reactivity of amalgam decreased markedly immediately after polishing. The clinical significance of this finding needs to be studied further.

**Conclusion**

The oxidative effect of oxidizing water on metallic restorative material was evaluated. A gold alloy, a platinum-supplemented gold alloy, a gold-silver-palladium, and two different amalgams were immersed in oxidizing water, NaCl-supplemented oxidizing water, or other solutions. Polarization curves were analyzed to examine the reduction profiles of oxidizing water and the following results were obtained:

1. The gold alloy and the platinum-supplemented alloy yielded similar polarization profiles. When these alloys were immersed in oxidizing water, no marked oxidation currents were seen at the corrosion potential level. Reduction waves of chlorine, hypochlorous acid, dissolved oxygen and hydrogen ions were seen in oxidizing water.

2. When the gold-silver-palladium alloy was immersed in oxidizing water, no marked oxidation currents were seen at the corrosion potential level, but silver chloride formation was seen. Reduction waves of hypochlorous acid and dissolved oxygen were seen in oxidizing water, but no hydrogen-ion reduction waves were isolated.

3. When conventional-type amalgam was immersed in oxidizing water, a polarization curve showing marked oxidation at a corrosion potential level was obtained. Reduction waves of hypochlorous acid were seen in oxidizing water. An increase in reduction currents associated with the reduction of hydrogen ions was noted. When high copper amalgam was immersed in oxidizing water, no marked oxidation currents were seen at the corrosion potential level. When the reduction profiles of high copper amalgam in oxidizing water were analyzed, reduction waves associated with hypochlorous acid were noted at more noble potentials, as compared to conventional type amalgam, but the other features of both amalgams were similar.

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**References**


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