

Galvanic Corrosion of Dental Amalgams in Contact with Titanium in Terms of Released Ions

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Galvanic corrosion between dental amalgams and titanium was examined in terms of released ions. The ions released from the dental amalgams in contact with titanium at surface area ratios of titanium/amalgam in a range of 1/10–10/1 were quantitatively analyzed after being immersed in 0.9 mass% sodium chloride solution at 310 K for 6.05×10^5 s. The potentials and the anodic polarization curves were also measured under the same conditions. Furthermore, the amalgam surfaces after immersion were analyzed using WDS. Each potential of the conventional amalgams was always lower than that of titanium, though each potential of the high-copper amalgam was reversed in the early stage of immersion and was also lower. When the surface area ratio did not increase to over 1/1, each total amount of ions released from the amalgams in contact with titanium was a little larger or smaller than that released from amalgams not in contact with titanium. However, tin and copper ions released from the conventional amalgams and the high-copper amalgam, respectively, increased greatly when the ratio grew to 10/1. Each amount of released ions with titanium, except mercury ions, was approximated by the equation $W_{\text{with}} = a \times (W_{\text{without}})^b$, where the coefficients "a" and "b" are constant and W_{with} and W_{without} mean each amount of the released ions with and without titanium, respectively. The coefficient "b" probably relied on the surface area ratio and immersion time. When the ratio grew to 10/1, the amount of released ions with titanium, except mercury ions, could be shown by the equation $W_{\text{with}} = a \times (W_{\text{without}})$ at $a = 4.202\text{--}9.982$. Since the contact with titanium seemed to drastically make the amount of mercury ions decrease, the mercury ions did not fit this equation. These results indicated a risk of galvanic corrosion between dental amalgams and titanium with a large surface area ratio.

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1. Introduction

Galvanic corrosion of dental amalgams has been noticed mainly in contact with gold alloys¹⁾ since the coexistence of dissimilar metals with largely different potentials creates the risk of a greatly increased amount of ions released from the metals through galvanic corrosion. Another reason for the increased risk is that galvanic pain derived from a galvanic current sometimes occurs in patients treated with a coexisting amalgam and gold alloy.²⁾

Holland³⁾ examined the galvanic current density between dental amalgams and a type IV gold alloy (ISO 1562). As the surface area ratio of the gold alloy in contact with the amalgams increased, the galvanic current density also increased on the conventional amalgam. However, the density of the high-copper amalgam without the γ_2 phase was always lower than that of the conventional amalgam and showed no influence independent of the surface area ratio. Johansson⁴⁾ also reported that the galvanic current density of a high-copper amalgam in contact with a gold alloy was lower than that of a conventional amalgam in whole saliva. Johansson and Moberg⁵⁾ tested ions released from a conventional lathe-cut amalgam in contact with a type III gold alloy (ISO1562). They reported that copper and tin ions were eluted more than silver, mercury and zinc ions and that the combination of the amalgam and the type III gold alloy remarkably increased the amount of released copper and tin ions.

On the other hand, with respect to amalgams in contact with titanium, which recently has been used for dental

appliances, most researchers seem to have focused on the behavior of the corrosion potentials and the galvanic currents.⁶⁾ Ravnholt⁷⁾ measured galvanic current densities between amalgams and titanium in 1 mass% sodium chloride solution and showed that the conventional and the high-copper amalgams preferentially corroded as anodes compared to titanium as a cathode. Johansson and Bergmanet⁸⁾ measured the galvanic current densities of amalgams in contact with titanium in 0.9 mass% sodium chloride solution and reported that the galvanic current was always anodic on the conventional amalgam. On a high-copper amalgam with titanium, the galvanic current was also anodic after enough time had passed to keep a steady state except at the early stage of immersion. Moreover, Horasawa *et al.*⁹⁾ examined the effects of surface area ratios of amalgam/titanium in a range of 1/1–1/6 on the corrosion potential and the galvanic current density on a high-copper amalgam in contact with titanium in artificial saliva at 310 K. Even when the titanium surface area increased, the galvanic current density scarcely rose, and there was no significant difference in the current densities in the range of 1/2–1/6.

Though the contact with the gold alloys or titanium seemed to cause a remarkable increase in the corrosion rate of the conventional amalgams, most high-copper amalgams in contact with titanium were optimistically assumed to maintain their corrosion resistance by only measuring the galvanic current densities in spite of the fact that an anodic situation was created. However, the anodic situation increases the risk that noxious ions hardly released in a single use could elute or that

released ions could increase even if a little corrosion damage occurred. Therefore, for amalgams which have been in oral cavities and have remained stable for a long time, contact with titanium prostheses poses more than a small risk. It is necessary to analyze the ions released from amalgams in contact with titanium in addition to measuring the galvanic current so as to accurately evaluate the safety of the amalgams for human tissues in present dental treatments.

The objective in this study is to investigate the effects of a surface area ratio of titanium/amalgam on the behavior of ions released from amalgams in contact with titanium and to evaluate the safety of a coexisting amalgam and titanium in the oral cavity. Conventional amalgams (Ag–25.8Sn–1.5Cu and Ag–27Sn–2Cu) and a high-copper amalgam (Ag–29Sn–16Cu) mixed with mercury were used. Ions released from conventional and high-copper amalgams in contact with titanium at surface area ratios of titanium/amalgam in a range of 1/10–10/1 were qualitatively and quantitatively analyzed after being immersed in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K for 6.05×10^5 s (7 days). The correlation of the ions released from each amalgam in contact or not in contact with titanium was also examined to determine the relation between an increasing rate of the release of ions and the surface area ratio of titanium/amalgam. Furthermore, corrosion potentials, galvanic corrosion currents and potentiodynamic polarization curves were measured under the same experimental conditions.

2. Materials and Methods

2.1 Materials

A conventional lathe-cut amalgam (Hi-Aristaloy: Heesung Engelhard Co., Ltd., Korea), a conventional spherical amalgam (Hi Atomic M: GC Co., Ltd., Japan) and a high-copper spherical amalgam (Lumi Alloy: GC Co., Ltd., Japan) were selected for this study since these three types of amalgams commonly have been used in dentistry. The compositions of the amalgam powders are shown in Table 1. The mass ratios of powder/mercury in Hi-Aristaloy, Hi Atomic M and Lumi Alloy were given as 1/1, 1/0.75 and 1/0.83, respectively, by the companies. After each of the amalgam powders was mixed with mercury in the mass ratio, columnar amalgam specimens in a diameter of 4 mm and a length of 10 mm were prepared in conformity with American National Standard/American Dental Association (ANSI/ADA) Specification No. 1 for Alloy for Dental Amalgam. These specimens were used for an elution test and for the other experiments after being kept at 310 K for 6.05×10^5 s. Half-size specimens for electrochemical measurements and surface analysis were made of a columnar amalgam cut in the median plane in the longitudinal direction and buried with an electrical lead in

epoxy resin. Titanium specimens were squarely cut off with sides measuring 10 or 30 mm from a rolled titanium sheet 1 mm thick (Grade 1: Kobe Steel Co., Ltd.).

2.2 Electrochemical measurements

Before being tested, each specimen surface was polished with 180–800 grit silicon carbide papers and then was ultrasonically cleaned with distilled water for 1 min. The amalgam specimen, of which the surface area was kept constantly at near 40 mm^2 , was electrically connected to the titanium specimen with an electrical lead after the titanium surface was adjusted with enamel resin so that the surface area ratio of titanium/amalgam became 1/10, 1/1 and 10/1 (“surface area ratio of titanium/amalgam,” hereafter referred to as “ $S_{\text{Ti}}/S_{\text{Am}}$ ”). The spacing between the amalgam and titanium specimens was set up at 5 mm. Potentials versus a reference electrode (Ag/AgCl) of each specimen, including the specimen not in contact, were recorded in 0.9 mass% sodium chloride solution with saturated dissolved oxygen (6.3 ppm) at 310 K for 6.05×10^5 s. Corrosion potentials were obtained by converting them to the standard hydrogen electrode (SHE). The galvanic current of the amalgams in contact with titanium with respect to each $S_{\text{Ti}}/S_{\text{Am}}$ was also measured using a zero-shunt ampere meter in the same condition. Statistical analyses of the corrosion potentials ($n = 3$) and the galvanic currents ($n = 3$) at 4.32×10^4 (12 h), 8.64×10^4 (24 h), 1.73×10^5 (48 h) and 6.05×10^4 s (168 h) were performed using ANOVA/Scheffe tests at a significance level of $p = 0.05$. After each specimen was immersed in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K for 1.73×10^5 s, the measuring of potentiodynamic polarization curves was begun. The potential scanned up from the rest potential to 1 V (SHE) at a rate of 5×10^{-4} V/s in the anodic polarization curves of the amalgams and also scanned down from the rest potential to -1 V (SHE) at the same rate in the cathodic polarization curve of titanium.

2.3 Elution test

The columnar amalgam specimen, the surface area of which was maintained at near 150 mm^2 , was electrically connected to the titanium sheet adjusted with $S_{\text{Ti}}/S_{\text{Am}}$ of 1/10, 1/1 and 10/1. The other conditions were similar to those of the specimen used for the electrochemical measurements. Each specimen, including the one not in contact, was immersed in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K for 6.05×10^5 s. The specimen was then removed from the solution and was qualitatively and quantitatively analyzed using the inductively coupled plasma atomic emission spectrometry analyzer (ICP) (IRIS_AP: Nippon Jarrell-Ash Co., Ltd., Japan). The mass per unit area of released ions was converted from the detected ion concentration. Statistical analyses of the released ions ($n = 5$) were also performed using ANOVA/Scheffe tests at a significance level of $p = 0.05$.

2.4 Surface analyses

After the corrosion potentials were measured, the surface morphology was observed using a scanning electron microscope (SEM) with wavelength dispersive X-ray spectroscopy (WDS) (JXA 8900R: JEOL, Japan). Corrosion products and

Table 1 Compositions of the amalgam powders (mass%).

Type of Amalgam	Product name	Ag	Sn	Cu	Rest
Conventional (Lathe cut)	Hi-Aristaloy	70.9	25.8	1.5	1.8
Conventional (Spherical)	Hi Atomic M	70.0	27.0	2.0	1.0
High copper (Spherical)	Lumi Alloy	55.0	29.0	16.0	—

the distribution of elements on each amalgam surface were qualitatively and quantitatively analyzed at an electron acceleration voltage of 15 kV. The amalgam powders and the amalgam surfaces before testing were also observed, and intermetallic compounds on the amalgam surfaces were identified. Statistical analyses of the distribution of elements ($n = 3$) were performed using ANOVA/Scheffe tests at a significance level of $p = 0.05$.

3. Results

3.1 Microstructure

SEM images of each amalgam powder tested in this study are shown in Fig. 1(a). Most particles of the conventional lathe-cut amalgam powder were larger than those of the other amalgams and showed a chips-like shape with a length exceeding 100 μm . Although large and small spherical particles with a diameter under 50 μm were blended in the conventional spherical amalgam powder, comparatively large particles with a diameter of 20–50 μm mainly constituted the high-copper amalgam powder.

Composition images of each microstructure of the amalgams admixed with mercury after being kept for 6.05×10^5 s at 310 K are also shown in Fig. 1(b). Both particle types of the conventional amalgams were composed of the remaining particle of the β (Ag–Sn) and the γ (Ag_3Sn) phases labeled P, the γ_1 (Ag_2Hg_3) phase labeled G1, which seemed to be the light gray matrix, the γ_2 (Sn_{7-8}Hg) phase labeled G2 and the ϵ (Cu_3Sn) phase labeled E in the figure.^{10,11} These phases exhibited the structures which had sufficiently proceeded the hardening reaction between the particles and mercury.^{10,11} The high-copper amalgam without the γ_2 phase was composed of the remaining particles of the β and γ phases, the γ_1 phase, the ϵ phase and the η' (Cu_6Sn_5) phase, labeled H in the figure.^{11,12}

The conventional spherical amalgam and the high-copper

amalgam seemed to have less quantity of the remaining particles of the β and γ phases than that of the conventional lathe-cut amalgam with large-size particles since the large surface area gained from the aggregation of small spherical particles accelerated to react with mercury.

3.2 Corrosion potential and galvanic current

Corrosion potentials of each amalgam and titanium in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K are summarized in Fig. 2. Typical profiles among the examined potentials were selected in the figure. Although the potential of titanium was close to that of both conventional amalgams right after immersion, it immediately rose with time and remained over 0.262 V and 0.234 V higher ($p < 0.05$) than those of the conventional lathe-cut and spherical amalgams, respectively after 1×10^5 s. The potential of both conventional amalgams tended to greatly increase with time after slightly dropping in the early stage of immersion,

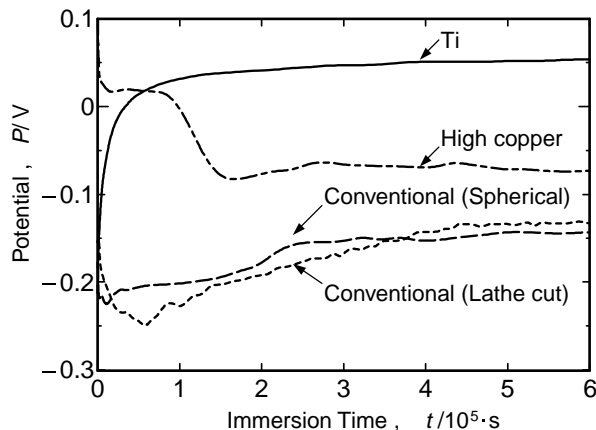


Fig. 2 Corrosion potentials of the amalgams and titanium in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K.

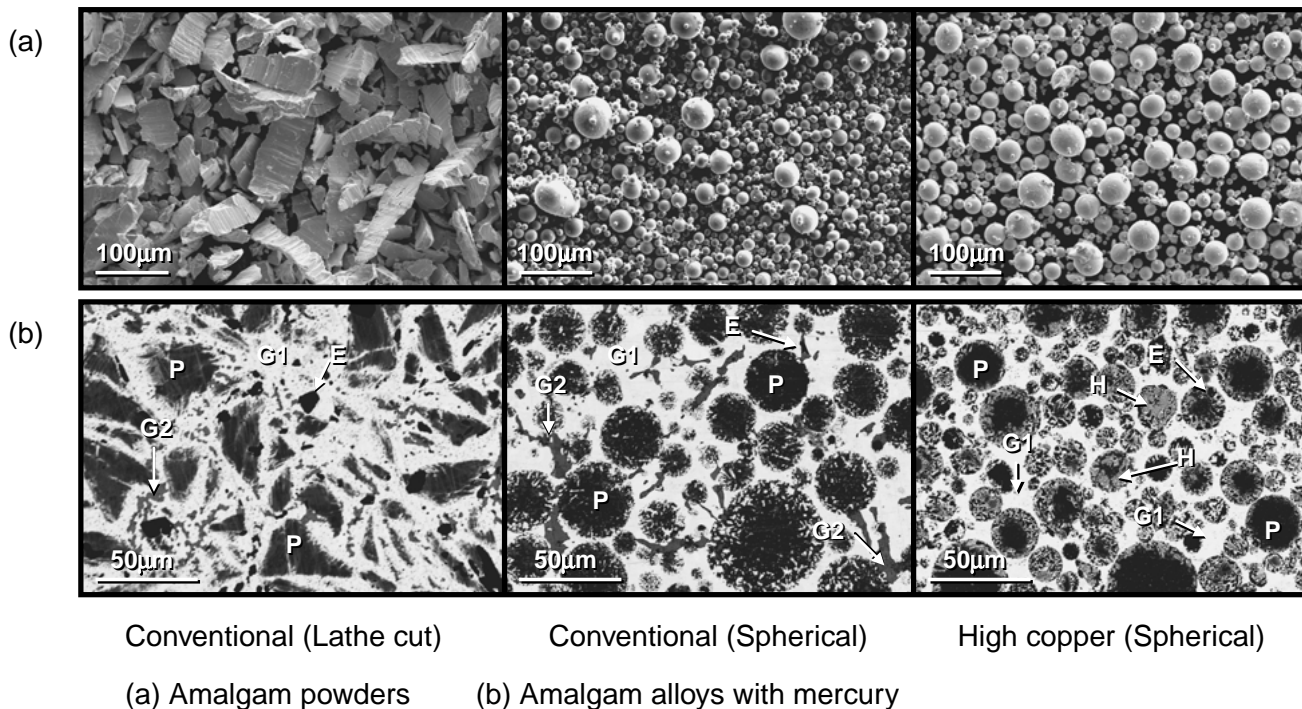


Fig. 1 The amalgam powders and microstructures of the amalgam alloys.

and it showed almost similar profiles. On the other hand, the potential of the high-copper amalgam was significantly higher ($p < 0.05$) than that of titanium in the early stage of immersion (for 4.32×10^4 s). However, the potential dropped down 0.096 V after 1×10^5 s had passed, and it was kept lower ($p < 0.05$) than that of titanium. The statistical analyses indicated that the potential of both conventional amalgams was significantly ($p < 0.05$) lower than that of titanium in each distribution. On the other hand, the potential of the high-copper amalgam was significantly ($p < 0.05$) higher than that of titanium at 4.32×10^4 s, insignificantly higher ($p > 0.05$) at 8.64×10^4 s and significantly ($p < 0.05$) lower at more than 1.73×10^5 s.

The average of corrosion potentials tended to increase slightly for both conventional amalgams in contact with titanium at $S_{Ti}/S_{Am} = 10/1$ compared to the ones not in contact. The averages of the conventional lathe-cut and spherical amalgams at 6.05×10^5 s showed -0.116 V and -0.140 V, respectively. However, the statistical analysis revealed no significant difference ($p > 0.05$) between each potential with and without titanium at any S_{Ti}/S_{Am} . Their galvanic currents always flowed from titanium to the amalgams independent of the S_{Ti}/S_{Am} . As might be expected, a large value of $S_{Ti}/S_{Am} = 10/1$ greatly increased the currents. The averages of the conventional lathe-cut and spherical amalgams at 6.05×10^5 s showed 0.141 A/m² and 0.0475 A/m², respectively. When the electrical charges that moved from titanium to the amalgams during the 6.05×10^5 s were summed up, the conventional lathe-cut amalgam showed 0.025 C/m² at $S_{Ti}/S_{Am} = 1/10$, 0.234 C/m² at $S_{Ti}/S_{Am} = 1/1$ and 0.737 C/m² at $S_{Ti}/S_{Am} = 10/1$. The electrical charges of the conventional spherical amalgam were slightly larger than the charges at each S_{Ti}/S_{Am} .

Although corrosion potentials made no significant difference ($p > 0.05$) in each high-copper amalgam except at $S_{Ti}/S_{Am} = 10/1$, the potential at $S_{Ti}/S_{Am} = 10/1$ was significantly lower ($p < 0.05$) than that of the others within 4.32×10^4 s. The galvanic currents, unlike those of the conventional amalgams, flowed from the amalgam to titanium in the early stage of immersion, and thereafter the current direction was reversed. In particular, the current direction at $S_{Ti}/S_{Am} = 1/10$ was reversed several times during the period of 1.73×10^5 s. The electrical charges moved from titanium to the amalgams for 6.05×10^5 s were 0.00127 C/m² at $S_{Ti}/S_{Am} = 1/10$, 0.0527 C/m² at $S_{Ti}/S_{Am} = 1/1$ and 0.658 C/m² at $S_{Ti}/S_{Am} = 10/1$.

3.3 Polarization curve

Anodic polarization curves of each amalgam and cathodic polarization curves of titanium after immersing for 1.73×10^5 s in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K are summarized in Fig. 3. The tenfold and tenth current densities of the cathodic polarization curve of titanium were added to the figure so as to support the cathodic reaction at $S_{Ti}/S_{Am} = 1/10$ or $S_{Ti}/S_{Am} = 10/1$. The anodic current started flowing at about -0.24 V and drastically increased on both conventional amalgams. Their slopes of current density against the potential were extremely large in Tafel's region. Two peaks were found at 0 V and 0.35–0.4 V on the conventional lathe-cut amalgam. Although three

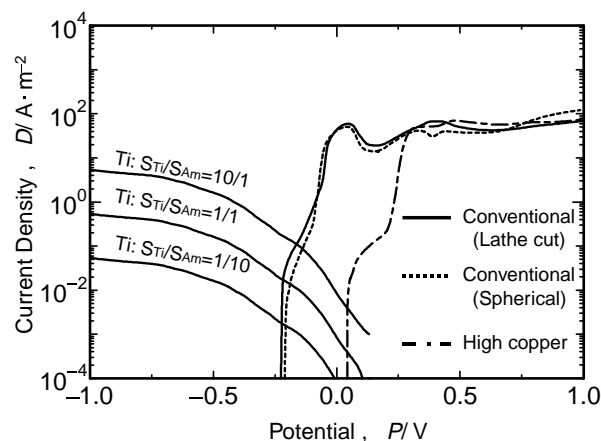


Fig. 3 Anodic polarization curves of the amalgams and cathodic polarization curves of titanium in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K.

peaks of the current density were found at 0 V, 0.3 V and 0.42 V on the conventional spherical amalgam, the profiles of both anodic polarization curves were almost similar. The anodic current started flowing at 0.04 V and also drastically increased on the high-copper amalgam. Two peaks were found at 0.3 V and 0.5 V, and after that, the current density gradually increased with the potential.

On the other hand, the cathodic current started flowing at 0.13 V and gradually increased with the negative potential on titanium in the cathodic polarization curve. Since an intersection point of the anodic and cathodic polarization curve indicates the corrosion potential and the galvanic current, these electrochemical values were obtained from Fig. 3. The potential and the current density increased by 0.06–0.09 V and 0.1 A/m², respectively, on both conventional amalgams at $S_{Ti}/S_{Am} = 10/1$ compared to the ones not in contact. In the high-copper amalgam, increases of 0.005 V and 0.004 A/m² were obtained. The contact with titanium could increase the corrosion potential of the amalgams as small as below 0.09 V.

3.4 Released ions

Amounts of ions released from the amalgams in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K during 6.05×10^5 s are shown in Fig. 4. The amounts of the ions released from the amalgams in contact with and not in contact with titanium are plotted on a logarithmic scale of the vertical and horizontal axes, respectively, and the correlation of the released ions with respect to each S_{Ti}/S_{Am} is shown. Since titanium could release ions below the detection limit in all cases, with or without contact with the amalgams, the amount of titanium ions is not shown in the figure.

The kinds of ions released from both conventional amalgams were silver, copper, mercury, indium and tin ions independent of the contact with titanium. Tin ions were mainly released from the lathe-cut and spherical amalgams without titanium, and the amounts of tin ions were 0.711 g/m² and 0.041 g/m², respectively. Though mercury ions (0.015 g/m²) were next in the lathe-cut amalgam, indium (0.023 g/m²) and mercury (0.004 g/m²) ions were ordered in turn in the spherical amalgam. The contact with titanium at $S_{Ti}/S_{Am} = 10/1$, which had the largest titanium surface area ratio in this study, caused the amount of tin ions to greatly increase in both con-

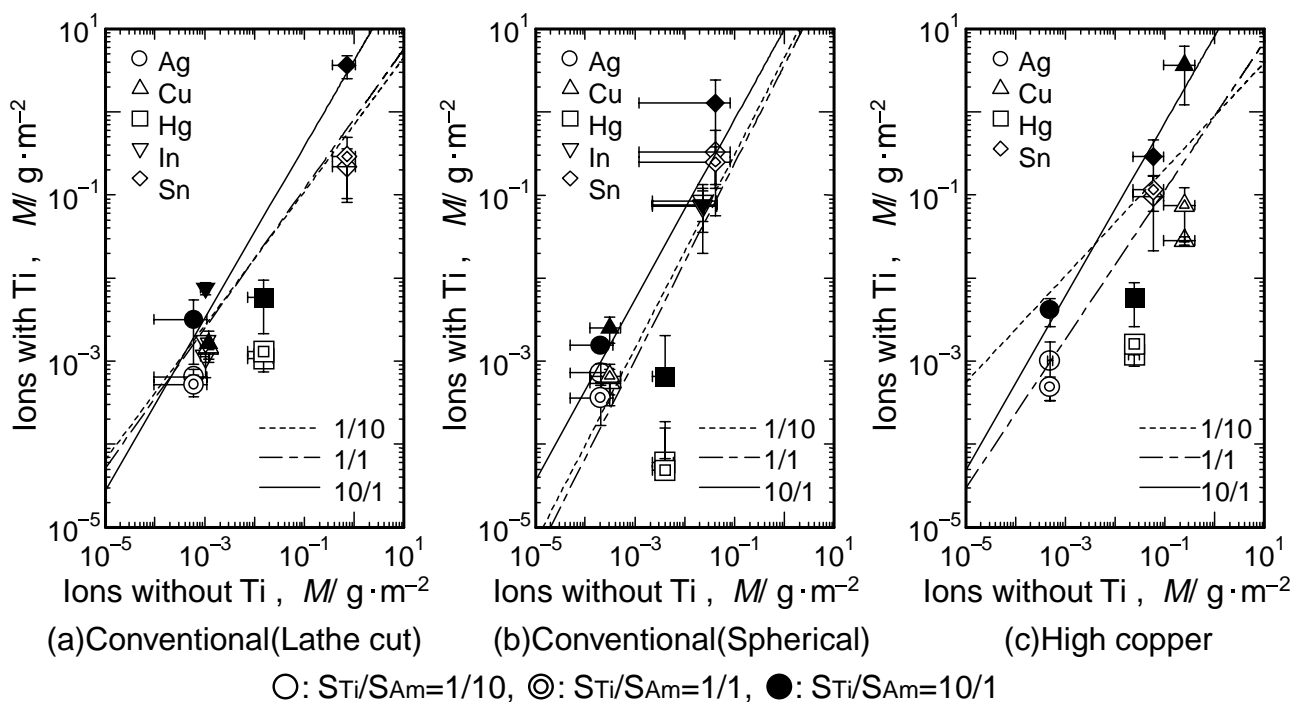


Fig. 4 Correlation of ions released from the amalgams contacted with and without titanium in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K during 6.05×10^5 s.

ventional amalgams. However, mercury ions decreased at any S_{Ti}/S_{Am} compared to the amalgams without titanium.

On the other hand, the kinds of ions released from the high-copper amalgam were silver, copper, mercury and tin independent of the contact with titanium. The order of abundance was copper (0.244 g/m^2), tin (0.058 g/m^2) and mercury ions (0.024 g/m^2). The contact with titanium at $S_{Ti}/S_{Am} = 10/1$ drastically increased the amount of not only copper ions but also tin ions. Mercury ions also decreased in a manner similar to that of the conventional amalgams.

The increasing and decreasing of the released ions and the average total amount of released ions are summarized in Table 2. As compared to the total amount of ions released from each amalgam without titanium, the amount released from the conventional lathe-cut amalgam was highest. Next was the high-copper amalgam, and the lowest amount was from the conventional spherical amalgam. For the amalgams in contact with titanium at $S_{Ti}/S_{Am} = 1/10$ and $1/1$, the total amounts of the released ions decreased in the conventional lathe-cut and the high-copper amalgams. However, the total amount increased in the conventional spherical amalgam but maintained the same order in the others. However, as the titanium surface area ratio increased at $S_{Ti}/S_{Am} = 10/1$, the total amounts of ions increased about 4–10 times more those of the amalgams without titanium.

Except for mercury ions, each amount of released ions, plotted on the logarithmic scale, tended to lie approximately in a straight line. When the amounts of the ions released from the amalgams with and without titanium are named W_{with} and $W_{without}$, respectively, the correlation between W_{with} and $W_{without}$ can be represented by eq. (1):

$$W_{with} = a \times (W_{without})^b \quad (1)$$

Here, the coefficients of “ a ” and “ b ” are constant. The co-

efficients of “ a ,” “ b ” and “ r ” (correlation coefficient) were obtained with respect to each S_{Ti}/S_{Am} , as summarized in Table 3.

3.5 Surface analysis

SEM images, including a composition image of each amalgam surface in contact with titanium at $S_{Ti}/S_{Am} = 10/1$ after being measured in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K, are shown in Fig. 5. A large quantity of corrosion products were observed on the surfaces of both conventional amalgams, as shown in Figs. 5(a) and (b). The analysis using WDS revealed that tin, oxygen and chlorine concentrated on the corrosion products. The larger value of S_{Ti}/S_{Am} allowed the deposit of a great quantity of corrosion products on the surface. Corrosion products were slightly observed on the surface of the high-copper amalgam, as shown in Fig. 5(c). However, the composition image shown in Fig. 5(d) indicates that dark areas, which are expected to have a different composition from the matrix, appeared in the vicinity of some small pits. The larger value of S_{Ti}/S_{Am} seemed to widely extend the dark areas.

The distribution of elements on the amalgam surfaces at $S_{Ti}/S_{Am} = 10/1$ before and after immersion is summarized in Table 4. Tin and oxygen concentrations were higher, and silver, copper and mercury concentrations were lower on the surfaces of both conventional amalgams after immersion compared to before immersion. The mercury concentration, especially, was greatly decreased. Since the concentration of elements distributed on the matrix of the high-copper amalgam after immersion was almost similar to that before immersion, the elements distributed on the dark areas are shown in the table. Tin, oxygen and chlorine concentrated on the dark areas, and silver, copper and mercury appreciably decreased compared to before immersion.

Table 2 Kinds of released ions and total amounts of released ions.

Amalgam	S_{Ti}/S_{Am}	Total amount, $M/g\cdot m^{-2}$	Kind of released ions ↑: Increase, ↓: Decrease
Conventional (Lathe cut)	Without Ti	0.729	Ag < In < Cu < Hg < Sn
	10/1	0.224	Ag < ↓ Hg < In < Cu < ↓ Sn
	1/1	0.297	Ag < ↓ Hg < Cu < In < ↓ Sn
	1/10	3.679	Cu < ↑ Ag < ↓ Hg < ↑ In < ↑ Sn
Conventional (Spherical)	Without Ti	0.068	Ag < Cu < Hg < In < Sn
	10/1	0.416	↓ Hg < ↑ Cu < ↑ Ag < ↑ In < ↑ Sn
	1/1	0.326	↓ Hg < ↑ Ag < ↑ Cu < ↑ In < ↑ Sn
	1/10	1.364	↓ Hg < ↑ Ag < ↑ Cu < ↑ In < ↑ Sn
High copper	Without Ti	0.328	Ag < Hg < Sn < Cu
	10/1	0.130	Ag < ↓ Hg < ↓ Cu < Sn
	1/1	0.194	Ag < ↓ Hg < ↓ Cu < Sn
	1/10	3.984	Ag < ↓ Hg < ↑ Sn < ↑ Cu

Table 3 Coefficients obtained from the released ions in the equation (1).

Amalgam	Coefficient	$S_{Ti}/S_{Am} = 1/10$	$S_{Ti}/S_{Am} = 1/1$	$S_{Ti}/S_{Am} = 10/1$
Conventional (Lathe cut)	<i>a</i>	0.711	0.834	4.202
	<i>b</i>	0.808	0.842	1.036
	<i>r</i>	0.999	0.994	0.979
Conventional (Spherical)	<i>a</i>	4.552	3.698	9.982
	<i>b</i>	1.167	1.184	1.086
	<i>r</i>	0.992	0.998	0.959
High Copper	<i>a</i>	0.902	0.902	8.293
	<i>b</i>	0.643	0.897	1.045
	<i>r</i>	0.884	0.957	0.988

4. Discussion

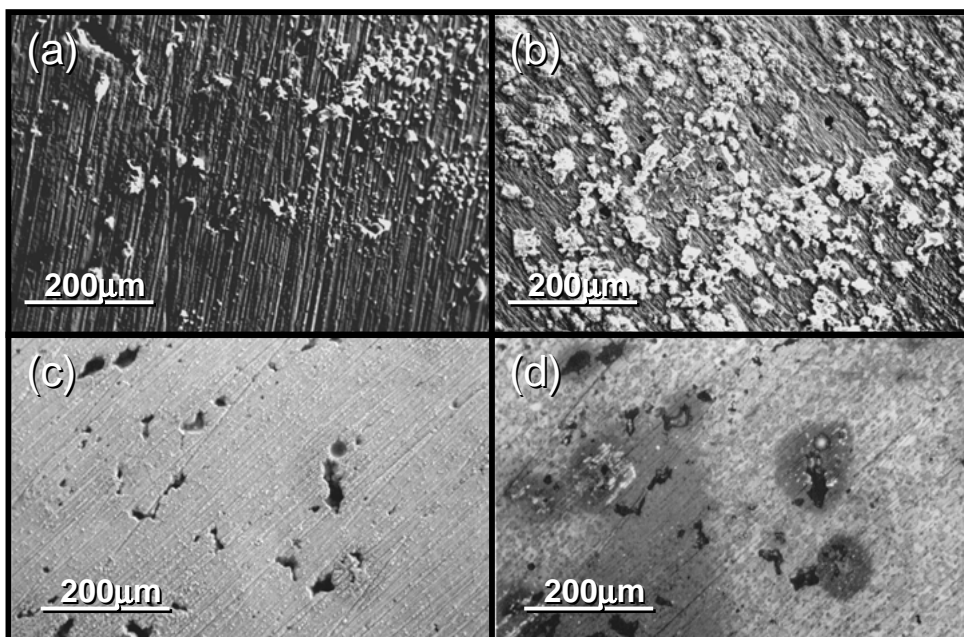
4.1 Preferentially dissolved phase

The structures of both conventional amalgams were composed of the remaining particles of the β (Ag–Sn) and γ (Ag₃Sn) phases, the γ_1 (Ag₂Hg₃) phase, the γ_2 (Sn_{7–8}Hg) phase and the ε (Cu₃Sn) phase, as shown in Fig. 1(b). Since the conventional spherical amalgam with the small particles could easily react with a small amount of mercury compared to the lathe-cut amalgam with the large particles,¹¹⁾ the quantity of remaining particles seemed to be relatively small in the spherical amalgam tested in this study. The structure of the high-copper amalgam was also composed of the remaining particles of the β and γ phases, the γ_1 phase, the ε phase and the η' (Cu₆Sn₅) phase. Since the copper and tin contained in the amalgam formed the η' phase, the γ_2 composed of tin and mercury disappeared in the structure.

The corrosive order of these phases in the amalgams is commonly known as follows: $\gamma_2 > \eta' > \gamma > \gamma_1 > \varepsilon$.^{1,10,11,13)} Marek¹⁾ revealed that the γ and the ε phases are thermodynamically more stable than either the γ_2 or η' phase. Onagawa and Abe¹³⁾ examined the electrochemical stability of each phase existing in conventional and high-copper amalgams using their anodic polarization curves in 0.9 mass%

sodium chloride solution. They reported that the peaks corresponding to the dissolution of the γ_2 phase, the γ phase, the γ_1 phase and the ε phase were found at 0 V, 0.3 V, 0.4 V and near 0.7–1.0 V, respectively.

Three peaks were found at 0 V, 0.3 V and 0.42 V in the anodic polarization curve of the conventional spherical amalgam, as shown in Fig. 3. These peaks at 0 V, 0.3 V and 0.42 V probably correspond to the dissolution of the γ_2 phase, the γ phase and the γ_1 phase, respectively. The conventional lathe-cut amalgam also represented two peaks at 0 V and 0.35–0.4 V. The overlapping of the peaks at 0.3 V and at 0.4 V appeared to make one wide peak at 0.35–0.4 V. The high-copper amalgam showed two peaks at 0.3 V and 0.5 V. These peaks also corresponded to the γ phase and the γ_1 phase, respectively. The corrosion potentials were placed within a range from –0.25 V to –0.15 V on both conventional amalgams independent of the contact with titanium. All potentials of the high-copper amalgam also were placed within a range from –0.05 V to 0.02 V. As shown in Fig. 3, these potentials were expected to exist in Tafel's region below the potential of the peak corresponding to the γ phase even if the amalgam was in contact with titanium at any S_{Ti}/S_{Am} tested in this study. According to the elution test, the amount of released tin ions was largest among the amounts of the other ions in



(a) Conventional (Lathe cut) (b) Conventional (Spherical)
(c) High copper (SEM) (d) High copper (Comp)

Fig. 5 The amalgam surfaces contacted with and without titanium at a surface area ratio of 10/1 in 0.9 mass% sodium chloride solution with saturated dissolved oxygen at 310 K after immersing during 6.05×10^5 s.

Table 4 Distributions of elements on the amalgam surfaces contacted with titanium at $S_{Ti}/S_{Am} = 10/1$ before and after immersion (Mean (S.D.), mass%).

	Conventional (Lathe cut)		Conventional (Spherical)		High Copper (Spherical)	
	Before	After	Before	After	Before	After
Ag	37.66 (4.51)	25.08 (6.38)	26.97 (2.49)	5.59 (1.51)	18.56 (0.62)	3.99 (3.07)
Cu	3.41 (0.52)	2.52 (0.47)	1.42 (0)	0.17 (0.11)	13.71 (1.60)	4.83 (1.53)
Hg	42.58 (6.05)	15.12 (9.50)	64.50 (1.55)	6.77 (1.17)	50.93 (1.56)	10.66 (7.22)
In	0 (0)	0 (0)	0.56 (0.04)	8.52 (2.61)	—	—
Sn	16.35 (2.21)	47.81 (11.91)	7.37 (1.13)	47.39 (8.59)	18.42 (0.49)	53.65 (8.25)
Cl	—	3.54 (3.29)	—	3.13 (2.21)	—	1.15 (0.96)
O	—	5.93 (1.29)	—	28.42 (3.97)	—	24.92 (3.24)

both conventional amalgams independent of the contact with titanium. The high-copper amalgam always mainly released copper and tin ions. Since both conventional amalgams and the high-copper amalgam released a small amount of silver or copper ions and mercury ions, respectively, a certain amount of the γ or γ_1 phase also naturally could dissolve. However, these results support the point that the contact with titanium scarcely changed the preferentially dissolved phases. Consequently, the γ_2 phase in both conventional amalgams and the η' phase in the high-copper amalgam probably dissolved preferentially¹⁴ even if the amalgams were in contact with titanium at any S_{Ti}/S_{Am} tested in this study.

4.2 Each amount of released ions

When each amount of ions released from the amalgams with and without titanium was named as W_{with} and $W_{without}$, respectively, the correlation between W_{with} and $W_{without}$ could be approximated by eq. (1), as mentioned before. The rela-

tion between the coefficient “ b ” shown in eq. (1) and S_{Ti}/S_{Am} is discussed here. Equation (1) can be changed to eq. (2) as follows:

$$\ln(W_{with}) - \ln(a) / \ln(W_{without}) = b \quad (2)$$

Equation (2) indicates that a logarithmic increasing rate of each amount of released ions is always a constant independent of the kind of ions. Since the coefficient “ b ” means a slope of the logarithmic increasing rate, 1 is substituted for the coefficient “ a ” in order to obtain the value of “ b ”. Equation (3) is obtained as follows:

$$\ln(W_{with}) / \ln(W_{without}) = b \quad (3)$$

If each amount of released ions is in proportion to current “ I ”, eqs. (4) and (5) are obtained as follows:

$$W_{with} = K \times I_{with} \quad (4)$$

$$W_{\text{without}} = K \times I_{\text{without}} \quad (5)$$

$$K = (M \times t)/(n \times F)$$

I_{with} : current with Ti I_{without} : current without Ti

M : atomic mass of the ion t : immersion time

n : number of electrons F : Faraday's constant

When eqs. (4) and (5) are substituted for eq. (3), eq. (6) is obtained:

$$b = \ln(K \times I_{\text{with}})/\ln(K \times I_{\text{without}}) \quad (6)$$

If the ions are assumed to mainly dissolve from the preferentially dissolved phase following Tafel's equation, the relation between overpotential " η " and current " I " represents eqs. (7) and (8):

$$\eta_{\text{with}} = B \times \ln(I_{\text{with}}) + A \quad (7)$$

$$\eta_{\text{without}} = B \times \ln(I_{\text{without}}) + A \quad (8)$$

η_{with} : overpotential with Ti

η_{without} : overpotential without Ti

A and B : constant

Equation (9) is obtained from eqs. (6), (7), (8) and (10):

$$b = (\eta_{\text{with}} + \eta_k)/(\eta_{\text{without}} + \eta_k) \quad (9)$$

$$\eta_k = B \times \ln(K) - A \quad (10)$$

Consequently, the coefficient " b " depends on a ratio of the overpotentials in contact with and not in contact with titanium and η_k containing the proportionality constant " K ". When the overpotentials are fixed by $S_{\text{Ti}}/S_{\text{Am}}$, " b " shows constant. If $S_{\text{Ti}}/S_{\text{Am}}$ is a large value, η_{with} becomes high, and " b " also becomes larger than 1. η_k depends on the constant " K " determined by the immersion time and the kind of elements, and it is affected by the constants A and B of Tafel's equation. If the immersion time is infinitely long, η_k infinitely grows, and " b " comes close to 1. In this case, " b " is always almost 1 even if η_{with} becomes high. The theoretical value of " b " keeps a range from $\eta_{\text{with}}/\eta_{\text{without}}$ to 1 ($0 < \eta_k < \infty$).

As compared with each coefficient of " a " and " b " shown in Table 3, all values of " b " are near 1 except for the high-copper amalgam at $S_{\text{Ti}}/S_{\text{Am}} = 1/10$. The experimental value of " b " seemed not to perfectly obey that theory. The values of " b " in all amalgams at $S_{\text{Ti}}/S_{\text{Am}} = 10/1$ were a little larger than those of the others. The large value of $S_{\text{Ti}}/S_{\text{Am}}$ seems to rise up the corrosion potential. When η_k was roughly estimated from the anodic polarization curves and immersion time in this study, it was below 0.1. η_k is possibly small for η_{with} at $S_{\text{Ti}}/S_{\text{Am}} = 10/1$, but it is large enough to affect the value of " b ". However, contact with titanium hardly affects the value of " b " except at $S_{\text{Ti}}/S_{\text{Am}} = 10/1$, since it increases the corrosion potential only a little. The value of " b " is almost 1 in the amalgams at $S_{\text{Ti}}/S_{\text{Am}} = 10/1$. Accordingly, eq. (1'), with only coefficient " a ," can represent each amount of the released ions.

$$W_{\text{with}} = a \times W_{\text{without}} \quad (1')$$

Equation (1') indicates that W_{with} is in proportion to W_{without} . For the coefficient " a ," the proportion constant appears to rely on the corrosion rate. If the value of " a " grows large,

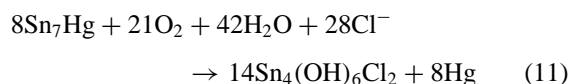
the contact with titanium makes the amount of the released ions increase. The values of " a " are arranged in ascending order as the conventional spherical (9.982), the high-copper (8.293) and the conventional lathe-cut (4.202) amalgams. Although contact with titanium would give the least increase to the conventional lathe-cut amalgam with the least value of " a ," the total amount of released ions is similar to that for the other amalgams because of the large amount of released ions without titanium, as shown in Table 2. Some reports of other measurements have revealed that a high-copper amalgam is superior to a conventional amalgam in the galvanic corrosion with titanium,^{6,9)} though the proportion constant " a " of conventional and high-copper amalgams at $S_{\text{Ti}}/S_{\text{Am}} = 10/1$ is almost the same in terms of the released ions. Note that both amounts of released ions increased approximately 10 times.

4.3 Decrease of released ions

Some kinds of released ions decreased in the amalgams at $S_{\text{Ti}}/S_{\text{Am}} = 1/10$ or $1/1$ compared to the amalgams without titanium, as shown in Table 2. Their coefficient " a " or " b " was below 1, and their total amount of released ions also decreased. Contact with titanium remarkably decreased the amount of mercury ions; therefore, the coefficients for mercury could not be shown in Table 3.

An attempt was made to examine the correlation of the amounts of released mercury ions in the amalgams with and without titanium. The amounts of released mercury ions were summarized with respect to each $S_{\text{Ti}}/S_{\text{Am}}$ in the calculation. The results showed that the correlation also could be approximated by eq. (1) in the correlation coefficient within 0.96–0.98. However, coefficient " a " was much smaller and " b " was larger than those of the other ions. The sets of values at $S_{\text{Ti}}/S_{\text{Am}} = 1/10$, $1/1$ and $10/1$ were $a = 0.034$ and $b = 1.762$, $a = 0.036$ and $b = 2.051$ and $a = 0.235$ and $b = 1.294$, respectively. Since mercury ions are assumed to dissolve unlike the other elements, the preferentially dissolved phases, the γ_2 and the η' , were noted in the dissolving reaction.

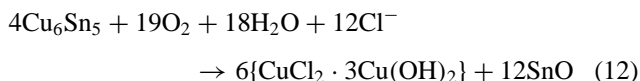
As shown in Table 4, tin increased, and silver, copper and mercury significantly decreased on the surface of the conventional amalgams with increasing values of $S_{\text{Ti}}/S_{\text{Am}}$. Probably the increase in tin was due to the covering of the surface with tin oxides or tin chlorides. Ogawa *et al.*¹⁵⁾ examined the charging and discharging curves of conventional and high-copper amalgams in 0.9 mass% sodium chloride solution and reported that most of the released tin ions existed as tin oxides on the surface of the amalgams. Marek¹⁾ also revealed that the γ_1 phases on an amalgam surface were covered with tin oxide films in the oral cavity. Generally, the γ_2 phase dissolves following eq. (11):¹¹⁾



This reaction indicates that the tin ions released from the γ_2 phase formed a complex salt with oxygen and chlorine and that mercury contained in the γ_2 phase formed mercury metal. Though part of the mercury metal changes to oxides and chlorides, the rest evaporates.¹⁶⁾ If the contact with titanium accelerated to dissolve the γ_2 phase, the amalgam surfaces would

be thickly covered with a large quantity of the corrosion products composed of tin. The accelerated dissolving of the γ_2 phase probably prevents the release of mercury ions from the amalgams.

In the high-copper amalgam, tin also significantly increased, and the other elements remarkably decreased in the vicinity of some small pits compared to the other areas on the surface. The η' phase existing in a high-copper amalgam dissolved following eq. (12)¹¹ and formed a tin oxide in addition to a tin complex salt with oxygen and chlorine:



The amalgam surface also was covered with the tin oxide and the tin complex salt, as described above. Covering the amalgam surfaces with the tin oxide and the tin complex salt during corrosion probably led to a decrease in the amount of released mercury ions. Since the high-copper amalgam acted as a cathode in the early stage of immersion, the amount of copper ions and mercury ions also decreased at $S_{\text{Ti}}/S_{\text{Am}} = 1/10$ and $1/1$.

4.4 Surface area ratio

When the surface area ratio, $S_{\text{Ti}}/S_{\text{Am}}$, did not go over $1/1$, each total amount of ions released from the amalgams with titanium was a little larger or smaller than that of the amalgam without titanium and showed a similar value. Contact with titanium makes mercury or copper ions decrease, which is better for avoiding metal allergies, which recently have been noticed. However, tin and copper ions released from the conventional and the high-copper amalgams, respectively, greatly increase if $S_{\text{Ti}}/S_{\text{Am}}$ greatly grows. High-copper amalgams, which have been the main amalgams used in recent dental treatments, show high clinical achievement, and electrochemical data have shown that there is no fatal damage caused by galvanic corrosion with titanium. Though the released ions revealed a risk of galvanic corrosion between small amounts

of amalgams, such as the amounts used in inlays, and large amounts of titanium, such as the amounts used in denture bases. The smallest possible surface area ratio of titanium to amalgam should be chosen so that the amalgam and titanium can safely coexist in the oral cavity.

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