

Evaluation of Corrosion Degradation of Amalgams by Immersion and Fracture Test

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In this study an immersion and fracture test was used to evaluate the susceptibility of dental amalgams to degradation of their mechanical strength by corrosion. Specimens of each of the six types of high-copper amalgams and one type of low-copper amalgam were prepared and tested. Cylindrical specimens were grooved using a diamond cutoff blade and immersed in 1% NaCl to which H₂O₂ was added to increase the oxidation power. After two weeks of exposure the specimens and controls were fractured and the loss of strength was calculated. Two amalgams showed a significant loss of strength. The test procedure is relatively simple and does not require sophisticated electrochemical or analytical instrumentation. A higher resolution power might be achieved by increasing the severity of corrosion or the number of replicate tests.

Key words : Amalgam, Corrosion, Fracture

INTRODUCTION

Corrosion by oral fluid weakens the amalgam structure. The most severe attack occurs in narrow gaps, such as between a filling and its tooth, where crevice corrosion takes place¹⁾.

Various techniques^{2–8)} have been used to evaluate the corrosion resistance of dental amalgams. Electrochemical techniques^{2–4)} such as potentiodynamic anodic polarization require skilled operators, sophisticated equipment, and interpretation of the data. Weight change tests and solution analysis^{5–8)} are not suitable for predicting the effect of corrosion on the mechanical properties of dental amalgams because of the formation of solid corrosion products, many of which are not released into the solution⁶⁾.

The aim of this study was to explore the use of an immersion and fracture test to evaluate degradation of the mechanical strength of dental amalgams of various chemical compositions. Test conditions included the formation of a crevice corrosion cell and the acceleration of the corrosion process by increasing the oxidation power of the electrolyte.

MATERIALS AND METHODS

Specimens were prepared from seven commercial amalgam alloys. They included two high-copper, single composition spherical alloys (D and F), one high-copper, single composition alloy containing indium (E), three high-copper admixed alloys (G, H and J) and one low-copper lathe-cut alloy (K). The codes, names, types and manufacturers are listed in Table 1.

The specimen preparation and test procedures are illustrated in Fig. 1. Cylindrical amalgam specimens (4 mm in dia. and 8 mm long) were prepared according to ANSI/ADA Specification No.1 and aged in air at 37°C for seven days. Each specimen was then grooved circumferentially at mid-length using a 0.3 mm thick diamond saw blade fitted to an electric dental engine (J. M. Uni Motor Type SR, Morita Co. Ltd., Tokyo, Japan) while the specimen was rotated in a lathe (EGURO PH6L, Eguro Co. Ltd., Nagano, Japan) at 300 rpm. The minimum diameter of the groove was measured.

From each set of specimens some were selected randomly for the corrosion exposure ($n=6$ to 8), and the remaining specimens were put back into the incubator as controls ($n=5$ to 7). A single loop of a white cotton thread, 60 tex (cotton count 10's), was wound lightly in the notch of each specimen selected for corrosion exposure and tied with a single knot. The thread was used to suspend the specimens in an exposure vessel containing a solution of 1% by weight of sodium chloride (NaCl) in deionized water.

The exposure vessels were then placed in a vacuum chamber and the air evacuated using a vacuum pump to 600 mm Hg or better for 5 min to remove air bubbles. Atmospheric air was then admitted into the chamber and the exposure vessels were stored in an incubator maintained at 37°C. After 24 hours of exposure, 3 ml of a fresh 30% solution of hydrogen peroxide (H_2O_2) per liter of the sodium chloride solu-

Table 1 Product names, types and manufacturers of tested amalgam alloys

Alloy	Product Name	Type	Manufacture	Composition of Powder (wt.%)				
				Ag	Sn	Cu	Zn	Other's
D	Tytin	High-copper Spherical Single composition	S.S. White, Ltd. Philadelphia, PA	60	28	12	—	
E	Indiloy	High-copper Spherical Single composition	Shofu Inc. Menlo Park, CA	59	24	13	—	In 4
F	Valiant	High-copper Spherical Single composition	L.D. Caulk Milford, DE	49.5	30.0	20.0	—	Pd 0.5
G	Dispersalloy	High-copper Admixed	Johnson & Johoson East Windson, NJ	69.3	17.9	11.8	1	
H	Phasealloy	High-copper Admixed	Phasealloy Inc. EI Cajon, CA	62.1	21.2	16.3	0.4	
J	Optaloy II	High-copper Admixed	L.D. Caulk Milford, DE	70.0	20.1	9.5	0.4	
K	Aristaloy	Low-copper Lathe-cut (irregular)	Baker Dental Carteret, NJ	69.1	26.5	3.8	0.6	

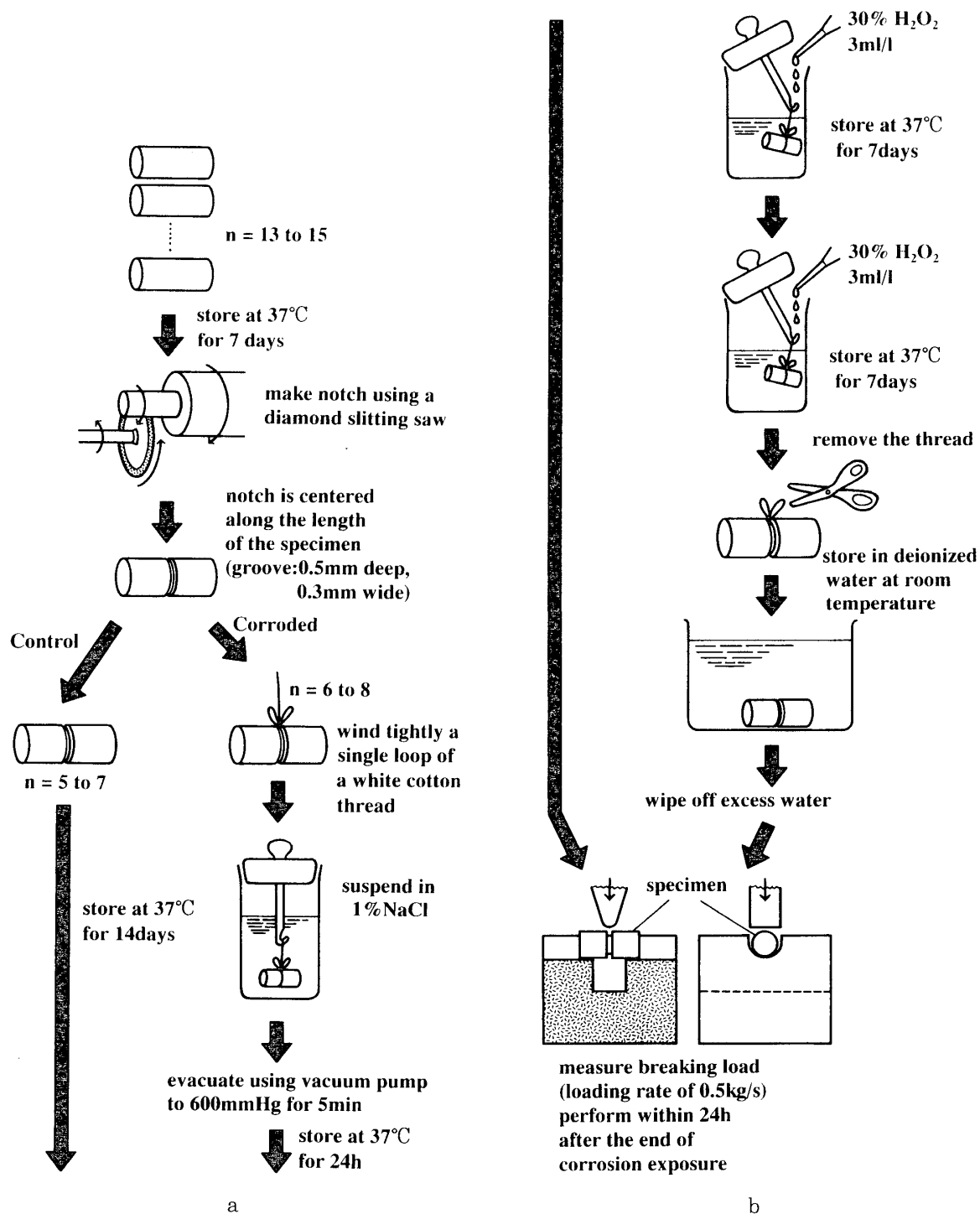


Fig. 1 Diagram of the test procedure for the immersion and fracture test.

tion was added to each exposure vessel. A similar addition of hydrogen peroxide was made after seven days of total exposure.

After 14 days of corrosion exposure both the controls and the corroded specimens were removed from the incubator. The corroded specimens were stored in deionized water at room temperature. Immediately before fracture testing excess

water was wiped off, but the specimens were not allowed to dry out.

The corroded specimens and controls were fractured in a three-point bending mode at a loading rate of 0.5 kg/s using a test machine (Autograph, Shimadzu Co. Ltd., Kyoto, Japan), and the breaking load $P_{\max}$ was determined. Fracture surfaces of the tested specimens were coated with gold using an ion-sputtering machine, and the area at the root of the notch was examined in an SEM (JCXA 733 Nihondenshi Co. Ltd., Tokyo, Japan).

The breaking stress values σ were calculated based on the actual specimen dimensions. The strength loss index (SLI) was calculated as follows:

$$\text{SLI} = [\{ \sigma(\text{control}) - \sigma(\text{corroded}) \} / \sigma(\text{control})] \times 100(\%)$$

The mean and standard deviation values of SLI for each was calculated based on the mean value of the breaking stress. The results for controls and corroded specimens were compared using the student's t-test ($p=0.05$) using a statistical software package (Excel Statistics, SRI, Tokyo Japan).

RESULTS

The groove was made with the dimensions and accuracy of 0.5 ± 0.05 mm in depth and 0.3 ± 0.05 mm in width.

The mean values of the breaking stress (MPa) and SLI are shown in Table 2. Amalgams E and K showed a statistically significant loss of strength. The mean strength loss index (SLI) for alloy G was negative (-45.9%), but the data dispersion was high and the difference was not statistically significant at $p \leq 0.05$.

Table 2 Fracture test results

Alloy	Breaking Stress (MPa) $\pm$ S.D. (C.V.)		SLI by the Mean of Breaking Stress (%)
	Control	Corroded	
D	159.3 $\pm$ 61.6 (38.7%)	127.9 $\pm$ 58.2 (45.5%)	19.7
E	166.0 $\pm$ 26.1 (15.7%)	108.4 $\pm$ 45.6 (42.1%)	34.7*
F	132.1 $\pm$ 57.3 (43.4%)	120.3 $\pm$ 38.8 (32.3%)	8.9
G	90.7 $\pm$ 48.0 (52.9%)	132.3 $\pm$ 33.7 (25.5%)	-45.9
H	165.1 $\pm$ 30.9 (18.7%)	152.0 $\pm$ 25.4 (16.7%)	7.9
J	179.4 $\pm$ 28.3 (15.8%)	161.8 $\pm$ 26.7 (16.5%)	9.8
K	213.5 $\pm$ 27.6 (12.9%)	167.8 $\pm$ 39.6 (23.6%)	21.0*

*Significant loss of strength at $P < 0.05$.

An SEM examination of amalgams D, F, H and J did not show apparent differences between the controls and corroded specimens. Figs. 2 and 3 show typical SEM micrographs of the fracture surfaces for the corroded specimens and controls of amalgams E and K, respectively. For amalgams E and K, corrosion products and evidence of a corrosion attack were found on specimens which had been exposed to the corrosive solution. A detailed examination in the SEM showed that the fracture of corroded specimens was often initiated at sites of corrosion damage. The fracture surfaces of the control specimens for amalgam E revealed a ductile manner of fracture with equiaxial dimples, while the corroded specimens showed evidence of a brittle fracture with cleavage (Fig. 2). The controls of amalgam K showed a mixed ductile/brittle fracture with cleavage mostly through the grains, while the corroded specimens exhibited a higher incidence of intergranular fracture (Fig. 3). The fracture surfaces of controls of amalgam G showed a mixed ductile transgranular and

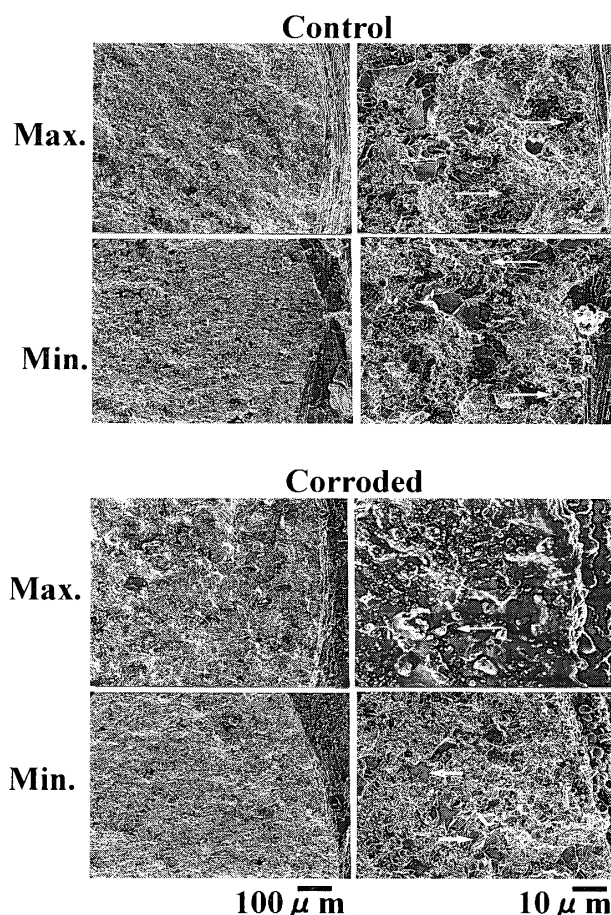


Fig. 2 SEM micrographs of fracture surfaces of controls and corroded specimens for alloy E. Codes Max and Min refer to the maximum and minimum of fracture strength values. Control: The arrow indicates equiaxial dimples. Corroded: The arrows indicate cleavage.

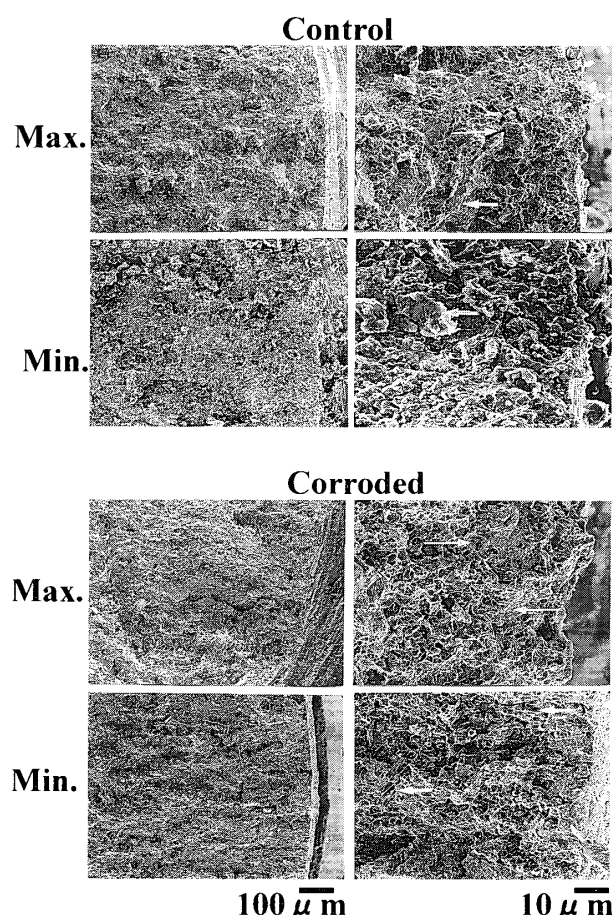


Fig. 3 SEM micrographs of fracture surfaces of controls and corroded specimens for alloy K. Code of Max and Min refer to the maximum and minimum of fracture strength values. Control: The arrows indicate cleavage. Corroded: The arrows indicate intergranular fracture.

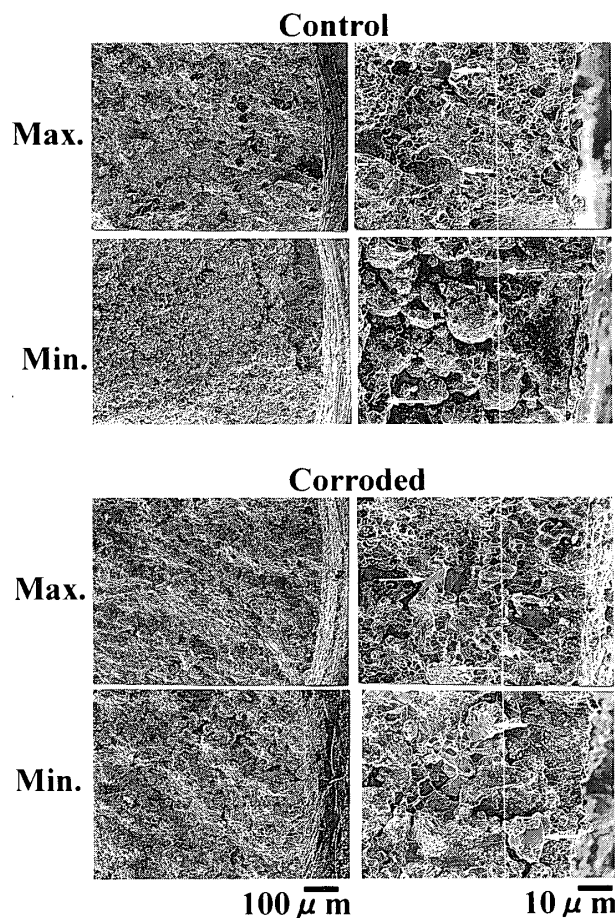


Fig. 4 SEM micrographs of fracture surfaces of controls and corroded specimens for alloy G. Code of Max and Min refer to the maximum and minimum of fracture strength values. Control: The arrows indicate ductile transgranular and intergranular fracture. Corroded: The arrows indicate cleavage.

intergranular fracture, while cleavage was often observed on the fractures of corroded specimens (Fig. 4).

DISCUSSION

Corrosion degradation of dental amalgam filling is most intensive in regions where corrosion is accelerated in the form of crevice corrosion, which involves the localized solution chemistry in the crevice becoming different from that of the outside. In this test crevice corrosion was induced in the groove cut of the specimens. Since the as-cut groove was too wide to be an effective crevice, tying cotton thread in the groove and thus impeding mass transport facilitated the occluded conditions. Evacuation of the solution was used to remove the air trapped in the cotton thread, which served

to slow down the ionic transport between the crevice and the outside.

Acceleration of corrosion in crevices is due mainly to acidification of the solution in the crevice, increases in the chloride ion concentration by migration of the chlorides to the region with a positive charge of dissolved ions, and the formation of oxygen concentration cells, with dissolved oxygen becoming depleted in the crevice. As acidification prevents the formation of protective oxides, the active metal surface becomes the anode of the cell, while the oxygen-rich surface on the outside becomes the cathode^{9,10}. Chlorides in the solution, the major aggressive ions in the oral environment, further destabilize the oxides⁹. In this study, the oxidation power of the solution increased with an addition of hydrogen peroxide (H_2O_2) to accelerate the cathodic kinetics outside of the crevice and thus increase the driving force for corrosion in the crevice.

When corrosion attacks a heterogeneous structure, the mechanical strength generally decreases. The mechanical part of the test was a simple measurement of the breaking load in a three-point bending mode and did not require skilled operators. No sophisticated electrochemical or analytical instrumentation was used, so the formation of corrosion products, which adversely affects weight change tests and tests involving solution analysis, was not a problem here.

Results of the tests were expressed as a percentage loss of strength (SLI). While all amalgams except one exhibited a loss of strength ranging from 8 to 35%, only the low-copper amalgam J (SLI=21) and a high-copper amalgam containing indium (alloy E, SLI=35) showed a statistically significant loss of strength when the results were analyzed at $p \leq 0.05$.

The examination of the fracture surfaces revealed more substantial differences between the corroded specimens and controls for amalgams E, G and K than for the other alloys, showing that corrosion had penetrated further into the interior in these amalgams, consistent with the observed degradation in fracture strength of amalgams E and K. An increase in brittle fracture features on the surfaces of the corroded specimens indicated that corrosion might result in an increase in stress concentrations. Amalgam K is a low-copper amalgam, containing the corrosion-prone γ_2 (Sn_8Hg) phase. Since the γ_2 phase forms a network through out the structure, the corrosion of this phase may have caused the observed increase in intergranular failure. Amalgam E, on the other hand, is an indium-containing amalgam in which indium was found distributed in the γ (Ag_3Sn) and γ_1 phases⁷. Since amalgam E is a γ_2 -free, high copper amalgam of the single composition alloy type, the strength degradation and apparent increase in brittle cleavage could be attributed to stress concentrations caused by corrosion of the η' (Cu_6Sn_5) phase in combination with the effect of indium on the properties of the γ_1 matrix.

The negative value of the SLI obtained for alloy G may have been due to statistical variation, such as the presence of random flaws in the unexposed controls. While corrosion often is a cause of stress concentrations, it is also conceivable that in some structures corrosion may cause a blunting of sharp discontinuities and thus increase resistance to fracture. In spite of the lack of a positive SLI for amalgam

G, the examination of the fractures of corroded specimens showed evidence in the corrosion of an increase in brittle fractures. A more specific explanation of the effects of corrosion on the strength of dental amalgams, especially for materials of the types E and G, will require a more thorough investigation.

Although the immersion and fracture test is relatively easy to conduct and provides information relevant to the performance of the amalgams in the oral environment, to make the test more discriminating will require an improvement in data dispersion and a higher acceleration of the corrosion process. Data dispersion may be lowered by improvements in specimen preparation, especially in cutting the groove, and the statistical significance can be improved by increasing the number of replicate tests. Higher acceleration of the crevice corrosion attack may be achieved by increasing the exposure time, more frequent additions of hydrogen peroxide, and by an increase in the concentration of chloride ions.

CONCLUSIONS

The immersion and fracture test is a promising test procedure for ranking dental amalgams with respect to their susceptibility to degradation in strength due to corrosion in oral fluids. In the present study the loss of strength results were obtained for seven commercial amalgams, and SEM examination of fracture surfaces confirmed that a crevice corrosion attack had occurred. Further improvements in specimen preparation and test procedure will be pursued to improve the predictive power of the test.

REFERENCES

- 1) Marek, M.: Treatise on materials science and technology "Corrosion: Aqueous processes and passive films", Academic Press, London, 1983, pp.331-334.
- 2) Boyer, D. B., Adey, J. D. and Fleming, M. A.: Mercury vaporization from corroded dental amalgam, *Dent Mater* 4: 89-93, 1994.
- 3) Marek, M.: Corrosion test for dental amalgam, *J Dent Res* 66: 63-69, 1980.
- 4) Horasawa, N., Nakajima, H., Ferracane, J., Takahashi, S. and Okabe, T.: Cyclic voltammetry of dental amalgams, *Dent Mater* 12: 154-160, 1996.
- 5) Okabe, T., Ferracane, J., Cooper, C., Matsumoto, H. and Wagner, M.: Dissolution of mercury from amalgam into saline solution, *J Dent Res* 66: 33-37, 1987.
- 6) Horasawa, N., Sugie, G., Ito, M. and Takahashi, S.: Electrochemical stability of dental materials "Part 4. Immersion test of amalgam", *J J Dent Mater* 8(1): 1-10, 1989. (in Japanese)
- 7) Mahler, D. B., Adey, J. D. and Fleming, M. A.: Hg emission from dental amalgam as related to the amount of Sn in the Ag-Hg (γ_1) phase, *J Dent Res* 73(10): 1663-1668, 1994.
- 8) Marek, M.: Dissolution of mercury from dental amalgam at different pH values, *J Dent Res* 76(6): 1308-1315, 1997.
- 9) Anusavice, K. J.: Phillip's science of dental materials, 10th ed, W.B. Saunders Co., Philadelphia, 1996, pp.347-358.
- 10) Unlig, H. H.: Corrosion and Corrosion Control, 2nd ed., John Wiley & Sons. Inc., New York, 1971, pp.71-75.