

Corrosion behavior of titanium in formic acid, oxalic acid, and formaldehyde

Tadafumi Kurogi, DDS,^a Shigeru Nakamura, DDS,^a Marie Koike, DDS, PhD,^a Motohiro Terano, DDS,^a Kunihiro Hisatsune, PhD,^b and Hiroyuki Fujii, DDS, PhD^a

^aDivision of Removable Prosthodontics and Management of Oral Function, and ^bDivision of Dental and Biomedical Materials Science, Department of Development and Reconstructive Medicine, Course of Medical and Dental Sciences, Graduate School of Biomedical Sciences, Nagasaki University, Nagasaki, Japan

Purpose: The purpose of the present study is to evaluate the influence of formic acid, oxalic acid, and formaldehyde on corrosion behavior of cast titanium.

Materials and Methods: Cast titanium specimens were immersed in 128 mmol/L formic acid, oxalic acid, and formaldehyde, and in 64 mmol/L oxalic acid for three weeks. Color change, weight loss, surface chemical binding state, and solubility of titanium were determined after immersion in the four solutions, and the changes in properties of the titanium surface were examined after immersion in 128 mmol/L oxalic acid.

Results: The discoloration of titanium specimens was significantly greater in formic acid than in either oxalic acid or formaldehyde. Both the weight loss and amount of titanium ions dissolved from specimens in oxalic acid were greater than the corresponding values after immersion in formic acid and formaldehyde. The superficial titanium oxide layer in post-immersion specimens was thickest in formic acid, followed by oxalic acid and formaldehyde.

Conclusion: The oxalic acid corroded titanium. The results may have important clinical implications for conditions such as titanium allergy and incompatibility. (*Int Chin J Dent 2006; 6: 1-7.*)

Key Words: corrosion, formaldehyde, formic acid, oxalic acid, titanium.

Introduction

Titanium is a useful biomaterial exhibiting chemical stability and higher level of biocompatibility, and it is implemented widely in dental restorations and medical implants.^{1,2} However, titanium dissolves in lactic acid and shows discoloration to a golden-yellow or purplish-blue color when immersed in formic acid.³ There have also been clinical reports regarding the discoloration and corrosion of titanium dentures.^{4,5} Much remains to be known about the elution and discoloration of titanium in vivo.

Formic acid, which causes the discoloration of titanium, is a deoxidizing organic acid that possesses aldehyde and carboxyl groups. It is considered to be strongly acidic, even among the carboxylic acids, and it is one of the acids promoting the growth of bacteria in the oral cavity. Formaldehyde possesses the aldehyde group, has a chemical structure similar to that of formic acid, undergoes oxidation to form formic acid, and is contained in certain dental medications. Moreover, oxalic acid, a dimer of the carboxyl group with oxidation-reduction potential, is an organic acid that is contained in many edible plants and forms formic acid when heated at high temperatures⁶ and corrodes titanium.⁷ A metabolic byproduct synthesized from glyoxylic acid, etc. in the body, oxalic acid is also present in saliva.⁸ As these facts indicate, titanium may come in contact with these substances in the oral cavity, and the observation of titanium's reaction thereto is essential to assess the properties of titanium as a biomaterial. The purpose of the present study is to conduct a comparative study on the reaction of titanium to formic acid, formaldehyde and oxalic acid.

Materials and Methods

Immersion solution

Formic acid, formalin (40% solution of formaldehyde and water), and oxalic acid (Wako Pure Chemical

Industries Ltd., Osaka, Japan) were prepared to serve as immersion test solutions. The three solutions were adjusted with distilled water to achieve the same mole fraction concentration as 1% lactic acid (128 mmol/L) used in previous study.³ Since oxalic acid is a dimer of the carboxyl group, a 64 mmol/L solution was also prepared. After adjustment, the pH of the solutions was 2.50 for formic acid, 4.00 for formalin, 1.33 for 128 mmol/L oxalic acid, and 2.55 for 64 mmol/L oxalic acid.

Preparation of titanium specimens

Specimens were cast from pure titanium (JIS2, Morita Corp., Tokyo, Japan; Ti) in approximately 15x20x1³ and 5x5x1 mm sizes according to the manufacturer's instructions. Five large and three small specimens were prepared for each immersion solution. The surface of the cast specimens was air-abraded using alumina powder of 50 µm in diameter. Next, the cast specimens were ground with #800 wet silicon carbide paper, subjected to ultrasonic cleaning in acetone for 15 minutes to remove grease, and stored in a desiccator. The large specimens were then used to measure changes in solubility, color and weight, while the small specimens were used to examine the chemical binding state of the specimen surface.

Immersion of specimens

Each specimen was entirely immersed in 10 mL of immersion solution contained in 50 mL centrifuge tubes, and lids were securely fastened on each tube. For each of the four immersion solutions, five tubes containing large specimens and three tubes containing small specimens, or a total of 32 tubes, were placed in an isothermal bath and shaken at a rate of 80 times/minute at 37°C for a period of three weeks. After three weeks, the specimens were removed from the tubes, subjected to cleaning in distilled water for 15 minutes and ultrasonic cleaning in acetone for 15 minutes, dried in a desiccator and used for the respective measurements.

Observation and analysis

Discoloration: The surface color of each dried specimen was examined macroscopically. Then a spectrophotometer (CM-503i, Minolta Co. Ltd., Tokyo, Japan) was used to measure the color at four sites selected randomly on each specimen, the mean measurement being considered the color value of the specimen. The light source, visual field angle and diameter were set at D65, 10° and 3 mm, respectively, and the color difference (ΔE^*_{ab}), that is, the difference between the measured color value and a standard value, was determined according to the L*a*b* colorimetric system.

Amount of dissolved ions: The amount of ions dissolved in each immersion solution was measured five times for each tube using inductively coupled plasma-atomic emission spectrometry (SPS-1700HVR, Seiko Instruments Inc., Chiba, Japan). The value was determined by dividing the measured amount by the surface area of the specimen, and by obtaining the amount of dissolved ions for each unit of area.

Weight changes: Specimens were weighed using an electronic analytical balance (AEM-5200, Shimadzu Co., Kyoto, Japan; readability=0.001 mg). The weight of the abraded, ground and dried specimens before immersion was compared with that of the cleaned and dried specimens after immersion, and the weight change per unit of area was determined by dividing the measured weight difference by the area of each specimen.

Depth analysis and microgeogram of the surface: We examined the chemical binding state of the surface of the small Ti specimens after immersion using an X-ray photoelectron spectrometer (ESCA-850, Shimadzu Co., Kyoto, Japan). Etching with argon ions was conducted repeatedly in the apparatus, and the depth of the chemical binding state was analyzed.³ MgK α (acceleration voltage, 8 kV; ion current, 30 mA) was used as the excited X-ray source for ESCA, and etching was conducted at 1 kV, 20 mA for 30 s. The specimen used for

analysis was the specimen judged by the corresponding author to have, among the three specimens, the closest approximation to a medium surface color on the basis of macroscopic evaluation.

To assess the extent of roughness and loss of gleam, we also examined the surface state of the specimens immersed in 128 mmol/L oxalic acid using a scanning electron microscope (S-3500N, Hitachi Co. Ltd., Tokyo, Japan).

Statistical analysis: We employed the one-way analysis of variance (ANOVA) for the statistical analysis. When a difference appeared to be significant, we also conducted multivariate variance analysis using Fisher's P.L.S.D.

Results

Discoloration

Fig. 1 shows variation of the color in large specimens before (control) and after immersion. The illustration on the far left shows a specimen prior to immersion (control). The four rows of five illustrations show, from top to bottom, the specimens immersed in 128 mmol/L formic acid, 128 mmol/L formaldehyde, and 128 mmol/L and 64 mmol/L oxalic acid solutions. In the 128 mmol/L oxalic acid specimens, weak golden-yellow discoloration was noted in all except the specimen second from the right, which showed a loss of gleam but no macroscopic discoloration. All of the specimens immersed in formic acid solution turned a golden-yellow color. The discoloration, however, was not necessarily uniform, some of the specimens showing a "mottled" or "shifting" pattern of discoloration.

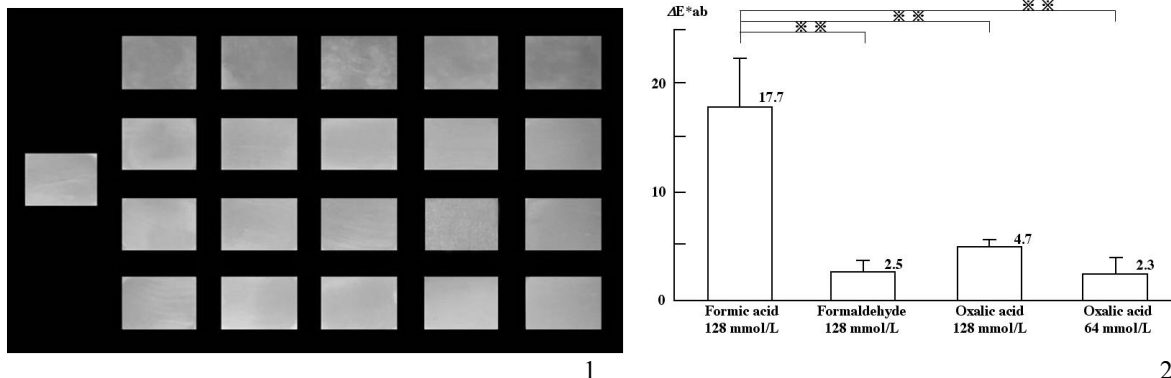


Fig. 1. Photographic presentation of titanium specimens.

The illustration on the far left shows a specimen prior to immersion (control). The four rows of five illustrations show, from top to bottom, the specimens immersed in 128 mmol/L formic acid, 128 mmol/L formaldehyde, 128 mmol/L oxalic acid, and 64 mmol/L oxalic acid solutions. Golden-yellow discoloration is evident in all of the formic acid specimens. In the 128 mmol/L oxalic acid specimens, weak golden-yellow discoloration was noted in all except the specimen second from the right, which showed a loss of gleam but no macroscopic discoloration.

Fig. 2. Discoloration of Ti specimens after immersion (color difference between controls and post-immersion specimens). Vertical axis, color difference ΔE^*ab ; Horizontal axis, four immersion solutions. The numbers and lines at the top of the graphs indicate the mean value and standard deviation, respectively. Asterisks, $p < 0.001$.

A graphic illustration on the color difference observed in the specimens after immersion (mean and SD) is presented in Fig. 2. The color difference (ΔE^*ab) between the specimens before and after immersion in formic acid solution was an average 17.7 (SD 4.25), a value that was significantly higher than that observed in the other three solutions ($p < 0.001$). With regard to the five specimens immersed in 128 mmol/L oxalic acid, four showed pale yellow discoloration and one a loss of gleam or pale gray color, the color difference being 4.7 (SD 0.73) in these specimens. The specimens immersed in the two remaining solutions were still silvery white in color, the

color difference being 2.5 (SD 0.78) and 2.3 (SD 1.28) for formaldehyde and 64 mmol/L oxalic acid, respectively. The extent of discoloration in these specimens was so low that it was impossible to discern macroscopically.

Dissolution

Fig. 3 shows the concentration of Ti ions dissolved in the immersion solutions. The concentration of Ti ions in the 128 mmol/L and 64 mmol/L oxalic acid solutions was 1.963 (SD 0.847) and 0.778 (SD 0.294) ppm/cm², values that were significantly higher than those observed in formic acid and formaldehyde. In fact, the Ti concentration observed in the formic acid solution was only 0.009 (SD 0.007) ppm/cm², and that observed in formaldehyde solution was so low as to be undetectable.

Weight loss

Fig. 4 presents the weight changes observed in the specimens. A slight increase was observed after immersion in formic acid solution (0.0009±0.0005 mg/cm²), while a decrease was observed in the 128 mmol/L and 64 mmol/L oxalic acid solutions (0.0262±0.0121 mg/cm² and 0.0116±0.0049 mg/cm², respectively). The weight change in the formaldehyde solution was negligible. A statistically significant difference was observed between the formaldehyde solution and the 128 mmol/L oxalic acid and formic acid solutions (p<0.05).

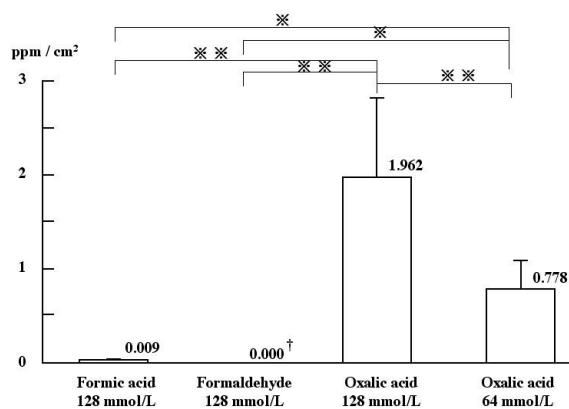


Fig. 3. Dissolution of Ti ions into immersion solution (ppm/cm²). Asterisk, p<0.05; Asterisks, p<0.001; Cross, Undetectable level.

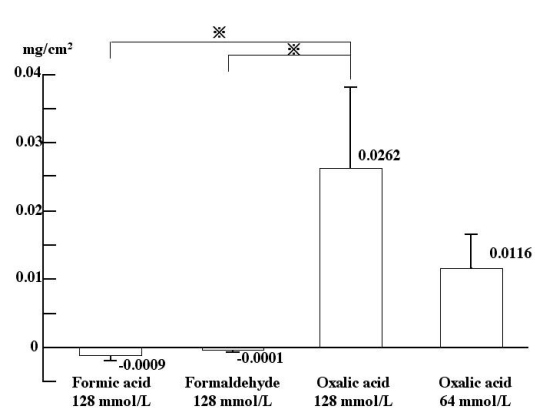


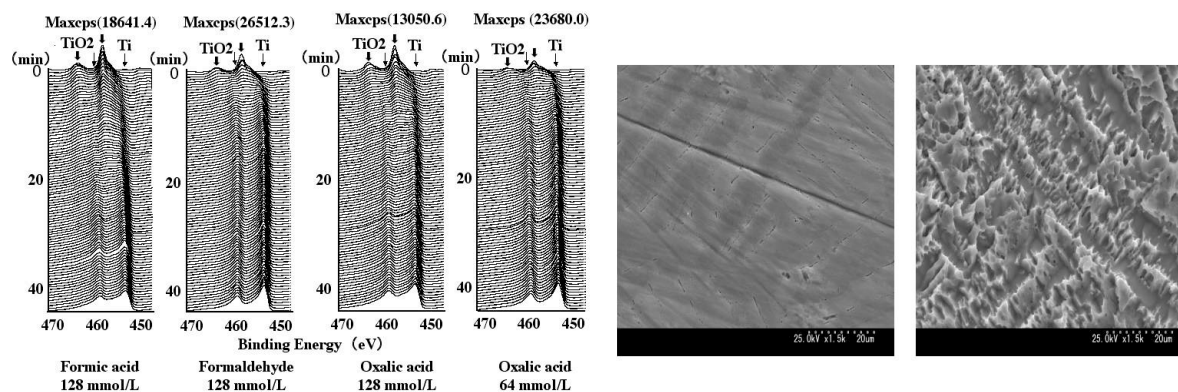
Fig. 4. Weight loss of Ti specimens after immersion (mg/cm²). Asterisk, p<0.05.

Depth analysis with ESCA

Fig. 5 presents the results of the analysis of chemical binding state of surface of small specimens after immersion using ESCA. On the first (superficial) layer and several lower layers of all specimens, peaks were observed near 459.1 eV and 464.8 eV,^{9,10} binding energies that correspond to titanium oxide. This layer was absent, and peaks appeared at 453.8 eV and 459.9 eV^{9,10} corresponding to metallic Ti, at the 74th layer in specimens immersed in formic acid, followed by the 60th layer in specimens immersed in 128 mmol/L oxalic acid, the 30th layer in specimens immersed in formaldehyde, and the 26th layer in specimens immersed in 64 mmol/L oxalic acid. The small specimens showed similar surface discoloration to the large specimens, and the appearance of a “mottled” pattern was observed slightly.

Microscopic surface state

Fig. 6 presents SEM images of a specimen before (control) and after immersion in 128 mmol/L oxalic acid solution (3rd row, 2nd column in Fig. 1). The post-immersion specimen surface shows an irregular series of grooves and ridges scattered with flat depressions and pinholes.



5

6

Fig. 5. ESCA images. The results of depth analysis with ESCA.

From among the three small specimens immersed in each solution, the specimen judged by macroscopic examination to have the closest approximation to a medium surface color was selected for analysis. Vertical axis, duration of etching; Horizontal axis, binding energy. The thin arrows indicate the position of metallic Ti (453.8 eV and 459.9 eV), while the thick arrows indicate the position of titanium oxide (459.1 eV and 464.8 eV).

Fig. 6. SEM images.

Left image is a specimen before (far left in Fig. 1), and right image is a specimen after immersion in 128 mmol/L oxalic acid solution (3rd row, 2nd column in Fig. 1).

Discussion

The immersion solutions used in the present study were formic acid, which discolors the surface of Ti,³ and oxalic acid and formaldehyde, two chemical substances made from the functional group that synthesizes formic acid. Formic acid is an organic acid that promotes the growth of resident bacteria in the oral cavity.¹¹ Oxalic acid is a metabolic byproduct of the oxidization of glyoxylic acid⁶ and an organic acid contained in large quantities in foods such as spinach, celery, oxalis and cocoa.¹² Formalin cresol, including formaldehyde, is used in endodontics.¹³ Therefore, Ti dental restorations in the oral cavity may be exposed to these three chemical substances. Needless to say, a variety of factors interact in the oral cavity, making it impossible, at the present time, to recreate the exact intra-oral conditions under which Ti is affected by these substances. Consequently, in view of the fact that formic acid is composed of two relatively simple functional groups, we decided to examine the corrosive effect of these functional groups on Ti in the present study. The concentration of immersion solutions was set at the mole fraction concentration of 1% lactic acid (128 mmol/L),³ which is used in metal discoloration,¹⁴ corrosion and immersion tests.^{15,16} We also prepared a 64 mmol/L solution of oxalic acid solution to make the volume of the carboxyl group equivalent to that of formic acid.

It is a well-known fact that the corrosion of metals is affected by pH.^{3,17} The pH of the immersion solutions used in the present study ranged from 1.33 to 4.00. The pH of many foods such as lemon juice and pickled plums also fall within this range,¹⁸ and some denture cleansing agents possessing the carboxyl group have a pH of 1 (Nishioka K. Personal communication). Aside from the effect of the buffering action that undoubtedly occurs in the oral cavity, the immersion solutions used in the present study can be considered to replicate the conditions encountered by denture users in their daily life and to provide appropriate experimental conditions for studies on the corrosion of Ti used as a dental biomaterial.

The surface color of Ti changes with the thickness of the oxidized layer on the surface of the specimen and also with the angle of examination. These phenomena are attributed to the refraction of light at the film-covered Ti surface.¹⁹ In the present study, all of the five specimens immersed in formic acid solution, and all of the five

specimens immersed in 128 mmol/L oxalic acid solution except one that lost its gleam, showed golden-yellow discoloration, and the extent of discoloration (Figs. 1 and 2) was greater the thicker the oxidized layer covering the specimen surface (Fig. 5).

A significantly greater release of Ti ions was observed in the oxalic acid solution than in either the formic acid or formaldehyde solution ($p < 0.001$; Fig. 3). In fact, the volume observed in 128 mmol/L oxalic acid solution (1.962 ± 0.847 ppm/ cm^2) was approximately four times that of lactic acid solution at the same concentration.²⁰ Furthermore, the changes observed in the weight of immersion specimens (Fig. 4) and in the surface state captured in SEM images (Fig. 6) provided evidence for the release of Ti ions in the oxalic acid solution or, in other words, for the occurrence of a corresponding level of hydrogen-induced corrosion. This would seem to indicate thinning of the oxidized layer on the surface of specimens after immersion in oxalic acid. Our results showed, however, that the oxidized layer was thicker after immersion in both 128 mmol/L and 64 mmol/L oxalic acid solutions (Fig. 5) compared with before immersion.³ This apparent contradiction can be explained by the fact that the surface of specimens immersed in oxalic acid solution under the conditions of the present study underwent greater hydrogen evolution type corrosion and even greater oxygen diffusion type corrosion than that observed in either lactic acid or formic acid solution.³

In the case of formaldehyde, the release of Ti ions in immersion solution was so low as to be undetectable, the weight of specimens increased slightly, and the thickness of the oxidized layer was only slightly thicker (10th layer)³ than that observed under the same conditions prior to immersion. These findings indicate that, although the corrosion of Ti specimens in formaldehyde is similar to that observed in formic acid solution, the degree of corrosion is obviously lower than that in formic acid.

The formic acid, formaldehyde and oxalic acid (which is found in salivary stones⁸ as well as in certain foods¹²) used in the present study are chemical substances that may come in contact with dental restorations in the oral cavity.

In conclusion, titanium corrodes oxalic acid and both hydrogen evolution type corrosion and oxygen diffusion type corrosion can occur titanium surface with chemical solutions of this study. This may have important implications for clinical practice in titanium allergy and incompatibility.²¹⁻²⁴

References

1. Yamauchi M, Sakai M, Kawano J. Clinical application of pure titanium for cast plate dentures. *Dent Mater J* 1988; 7: 39-47.
2. Laing PG, Ferguson AB Jr, Hodge ES. Tissue reaction in rabbit muscle exposed to metallic implants. *J Biomed Mater Res* 1967; 1: 135-49.
3. Koike M, Fujii H. The corrosion resistance of pure titanium in organic acids. *Biomaterials* 2001; 22: 2931-6.
4. Sutton AJ, Rogers PM. Discoloration of titanium alloy removable partial denture: A clinical report. *J Prosthodont* 2001; 10: 102-4.
5. Abe T, Matsumoto M, Oda Y, et al. Discoloration of titanium induced by denture cleaner. *J J Dent Mater* 2001; 20: 366-71.
6. Hodgkinson A. Determination of oxalic acid in biological material. *Clin Chem* 1970; 16: 547-57.
7. Kouyama T. Titanium design data book. Titanium metals corporation of America. 8th ed. Tokyo: Japan Titanium Society; 1995. p. 18-9.
8. Omori H, Sakakibara T, Okabe K, Inagaki K, Yamada S, Nakashizuka T. Oxalic acid and calcium levels in salivary stone. *J J Periodontol* 1986; 28: 176-8.
9. Ramqvist L, Hamrin K, Johansson G, Fahlman A, Nordling C. Charge transfer in transition metal carbides and related compounds studied by ESCA. *J Phys Chem Solids* 1969; 30: 1835-47.
10. Porte L, Demosthenous M, Duc TM. Étude ESCA de l'interaction oxygène-titane. *J Less-common Met* 1997; 56: 183-91.
11. Distler W, Kröncke A. Formic acid in human single-site resting plaque-quantitative and qualitative aspects. *Caries Res* 1986; 20: 1-6.
12. Konrad D. *Documenta Geigy Scientific Tables*. 6th ed. Basle: JR Geigy S.A.; 1962. p. 501-13.
13. Ingle JI. *Endodontics*. 3rd ed. Philadelphia: Lea & Febiger; 1985. p. 566-74.
14. Horibe T, Wakumoto S, Sato H. Studies on discoloration of dental alloys PART 2. Color and weight changes of dental alloys in mouth. *J J Dent Mater* 1967; 16: 29-34.
15. Speck KM, Fraker AC. Anodic polarization behavior of Ti-Ni and Ti-6Al-4V in simulated physiological solutions. *J Dent Res* 1980; 59: 1590-5.

16. Matsuno S. A study on corrosion of dental titanium alloys. *Shikwa Gakuho* 1987; 87: 1141-52.
17. Wataha JC, Lockwood PE, Khajotia SS. Effect of pH on element release from dental casting alloys. *J Prosthet Dent* 1998; 80: 691-8.
18. McCabe JF. *Applied dental materials*. 8th ed. London: Butler & Tunner Ltd; 1990, p. 1-28.
19. Cotton JB, Hayfield PCS. Decorative finishes on titanium. *Trans Inst Metal Finishing* 1967; 45: 48-52.
20. Koike M, Nakamura S, Fujii H. In vitro assessment of release from titanium by immersion tests. *J Jpn Prosthodont Soc* 1997; 41: 675-9.
21. Fujii H, Nakamura S, Koike M, et al. Metal allergy – in terms of dental practice -. *DE* 1997; 120: 1-5.
22. Basketter DA, Whittle E, Monk B. Possible allergy to complex titanium salt. *Contact Dermatitis* 2000; 42: 310-1.
23. Lalor PA, Revell PA, Gray AB, Railton GT, Freeman MAR. Sensitivity to titanium. A cause of implant failure?. *J Bone Joint Surg Br* 1991; 73: 25-8.
24. Peters MS, Schroeter AL, Van Hale HM, Broadbent JC. Pacemaker contact sensitivity. *Contact Dermatitis* 1984; 11: 214-8.

Correspondence to:

Dr. Tadafumi Kurogi
Division of Removable Prosthodontics and Management of Oral Function
Department of Development and Reconstructive Medicine
Course of Medical and Dental Sciences, Graduate School of Biomedical Sciences, Nagasaki University
1-7-1, Sakamoto, Nagasaki 852-8588, Japan
Fax: +81-95-849-7694 E-mail: kurofumi@net.nagasaki-u.ac.jp

Received November 29, 2005. Revised December 19, 2005. Accepted December 26, 2005.
Copyright ©2006 by the *International Chinese Journal of Dentistry*.