Corrosion Characteristics of α -Ti and Ti₂Cu Composing Ti-Cu Alloys

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Received July 21, 2005/Accepted October 4, 2005

A series of binary Ti-Cu alloys containing 5–20 mass% Cu was prepared, and the corrosion behavior of α -Ti and Ti₂Cu composing the Ti-Cu alloys were examined based on the anodic polarization curves and released ions in 0.9% NaCl and 1% lactic acid solutions. In both solutions, the Ti-Cu alloys showed the same anodic polarization curves as titanium in the condition below 1.4 V. However, precipitation of Ti₂Cu contributed to a small increase in current density in the transpassive region beyond 1.4 V. The amount of Cu ions released from Ti₂Cu was 0.260 and 1.003 ($\mu\text{g}/\text{cm}^2/7$ days) in 0.9% NaCl and 1% lactic acid solutions respectively. Although these values were larger than those from α -Ti (0.0379 ± 0.0041 and 0.0962 ± 0.0327 ($\mu\text{g}/\text{cm}^2/7$ days) in NaCl and lactic acid solutions respectively), they were not greater than those from type 4 gold alloy under the same conditions.

Key words: Elution test, Corrosion, Ti-Cu alloy

INTRODUCTION

Owing to its wide solid-solution β -Ti phase region, alloying titanium with β stabilizing elements is believed to decrease its fusion temperature and to improve its mechanical properties. Therefore, many researchers have studied the mechanical properties^{1–4)}, corrosion behavior^{5–7)}, and castability^{8,9)} of binary titanium alloys containing β stabilizers with a view toward their practical applications in dental appliances. Okuno *et al.*¹⁰⁾ found that experimental binary titanium alloys containing β stabilizers could retain a metastable β -Ti phase at room temperature, and were hence a potential material for dental casting. Takemoto *et al.*¹¹⁾ also focused on Ti-Cr alloys with a metastable β -Ti phase and revealed that their resistance to corrosion by fluoride ions was superior to that of titanium.

Attempts have been made to utilize α -Ti phase and intermetallic compounds in binary titanium alloys containing Ag or Cu, which is a β stabilizer, to improve the grindability and machinability of titanium^{12,13)}. Titanium alloyed with Cu cannot retain a β -Ti phase at room temperature despite cooling by water quenching, and it commonly has a α -Ti phase or α -Ti and Ti₂Cu phases which precipitate by means of an eutectoid reaction⁵⁾. Kikuchi *et al.*³⁾ noted that a series of binary Ti-Cu alloys containing 2–10 mass% Cu had a matrix of the α -Ti phase, and that a Cu content beyond 5 mass% precipitated the Ti₂Cu phase in the matrix. Takahashi *et al.*²⁾ examined the microstructures and mechanical properties of a series of binary Ti-Ag or Ti-Cu alloys containing 2–20 mass% Ag or Cu respectively. They also revealed that all of the alloys had matrices of the α -Ti phase, and that alloying with 20 mass% Ag or 10 mass%

Cu induced the Ti₂Ag or Ti₂Cu phase respectively in their matrices. Furthermore, they noted that Ti-Cu alloy containing 5 mass% Cu showed sufficient elongation (over 6%) and tensile strength (about 700 MPa) for use in partial dentures.

Shimizu *et al.*¹⁴⁾ examined the castability of binary Ti-Cu alloys containing 1 or 4 mass% Cu using two different wedge-shaped molds. They reported that Ti-Cu alloys showed as good castability as titanium and were also acceptable for clinical use. Kikuchi *et al.*¹⁵⁾ showed that the grindability of Ti-Ag and Ti-Cu alloys containing 20 mass% Ag and 5–10 mass% Cu, respectively, was superior to that of titanium. They also revealed that titanium alloyed with 20 mass% Ag or 5 mass% Cu showed promise for use as a free-machining titanium alloy in dental CAD/CAM systems because of its mechanical properties since the intermetallic compound of Ti₂Ag or Ti₂Cu phase helped to improve the grindability. Clearly, Ti-Cu alloys show potential for use as new dental titanium alloys that can be shaped by casting and dental CAD/CAM systems.

While titanium alloys are believed to show improved mechanical properties, castability, grindability, and other favorable features, corrosion resistance is sometimes reduced. The authors have already reported that titanium alloyed with β stabilizing elements of 5–30 mass% Ag, Cu, Co, Cr, Fe, Mn, or Pd showed anodic polarization curves similar to that of titanium under electrochemical oxidation below 1.8 V in 0.9% NaCl solution. Exception arose when titanium was alloyed with at least 20 mass% Ag⁵⁾. However, Oda *et al.*⁶⁾ reported that alloying titanium with Cu at a content range of 5–40 at% reduced the corrosion resistance and transpassive potential of titanium in artificial saliva. Unfortu-

nately, the contradictions between these reports have not been resolved yet. Although it is known that titanium and titanium alloys can dissolve more easily in lactic acid solutions than in other solutions used for dental corrosion tests^{16,17}, there is insufficient information on the released ions and electrochemical properties of Ti-Cu alloys in lactic acid solutions. To make matters worse, few recent studies have focused on ions released from Ti-Cu alloys, which is an important issue in regard to their safe use in human tissue.

As described above, while alloying with Cu improves the mechanical properties and grindability of titanium, an alloy composition in which the α -Ti and Ti₂Cu phases coexist must be chosen. Most intermetallic compounds often contain a factor which reduces corrosion resistance. For example, Cr₂₃C₆ and σ phase (FeCr) induce intergranular corrosion in austenitic stainless steel^{18,19}. Therefore, the electrochemical properties and amount of released ions of not only complete Ti-Cu alloys, but also of α -Ti and Ti₂Cu phases composing them, should be investigated in detail. Further, the investigation must be done with a view to ensuring not only the clinical safety of Ti-Cu alloys for dental use, but also that of the Ti₂Cu phase.

In this study, a series of Ti-Cu alloys containing 5-20 mass% Cu was experimentally prepared, and microstructural observation and X-ray diffractometry of the alloys were performed. Potentio-dynamic anodic polarization curves were measured, and ions released from the alloys were qualitatively and quantitatively analyzed in 0.9% NaCl and 1% lactic acid solutions, which are often used for dental corrosion tests²⁰. The objective was to estimate the individual electrochemical stability of both α -Ti and Ti₂Cu phases, and to investigate the dissolution of ions from each phase in both solutions.

MATERIALS AND METHODS

Materials

After titanium sponges (>99.8 mass%) were melted using an argon arc melting furnace (TAM-4S, Tachibana Riko Co., Ltd.) with a vacuum level below 5×10^{-5} torr, the resultant titanium buttons were cut into slices. A button of Ti-Cu alloy containing 5, 10, 15, or 20 mass% Cu was prepared by melting pieces of a titanium slice and a copper sheet (>99.999 mass%) using the argon arc melting furnace under the same conditions. (Ti-5, 10, 15, or 20 mass% Cu alloy will hereafter be referred to as 5Cu, 10Cu, 15Cu, or 20Cu alloy respectively.) To ensure homogeneity, the button (30 g) was inverted six times during the melting process. The titanium button was used as a control.

Methods

Buttons of each Ti-Cu alloy and titanium were cast according to the manufacturer's instructions into two thin plates (10 mm square $\times$ 2 mm thick and 15 mm long $\times$ 10 mm wide $\times$ 2 mm thick) using magnesia investment molds (Selevest CB, Selec Co., Ltd., Japan) at 200°C on a centrifugal casting machine with an argon arc melting system (TICAST Super R, Selec Co., Ltd., Japan). The square and rectangular cast specimens were used for microstructural observation, electrochemical evaluation, and elution test.

Microstructural observation of titanium and Ti-Cu alloys was performed using an electron probe microanalyzer with WDS (JXA8900, JEOL, Ltd., Japan). Composition images (reflection electron images) were selected because the alloys were observed without chemical etching so as not to lose intermetallic compounds or other precipitates. X-ray diffractometry (X'pert-MPD PW3050, Philips Co., Ltd., Netherlands) was also employed using CuK α radiation at 40 kV and 40 mA with a scanning rate of 0.25°/sec. Phase identification was carried out by matching each characteristic peak with the JCPDS file (1998).

After specimens of each Ti-Cu alloy and titanium were polished with #180-800 grit emery papers and ultrasonically cleaned in distilled water for one minute, electrochemical evaluation was carried out. The potentio-dynamic anodic polarization curve of each specimen was measured in 0.9% NaCl or 1% lactic acid solution with less than 0.2 mg/L dissolved oxygen ($n=3$). Scanning potential was from rest potential to 1.8 V (vs. NHE) at a rate of 0.5 mV/sec.

For the elution test, specimens of each Ti-Cu alloy and titanium were prepared with five sheets per alloy composition. Surface condition was the same as that used for the above-mentioned measurement of anodic polarization curves. Each specimen was immersed in 10 ml of 0.9% NaCl or 1% lactic acid solution with saturated dissolved oxygen (6 mg/L) at 37°C for seven days ($n=5$). After each specimen was removed from the solution, the released ions were analyzed qualitatively and quantitatively using ICP (IRIS_AP, Japan Jarrel Ash Co., Ltd., Japan).

Statistical analyses of ions released from each alloy and titanium were performed using ANOVA (Scheffe's test) at a significance level of $p=0.05$.

RESULTS

X-ray diffraction patterns of the Ti-Cu alloys and titanium are shown in Fig. 1. The patterns of titanium and 5Cu alloy completely matched that of α -Ti, but no peaks corresponding to those of Ti₂Cu could be found. However, peaks corresponding to Ti₂Cu appeared in the pattern of α -Ti composing the 10Cu alloy, and the peaks tended to be enhanced as the Cu content increased. X-ray diffractometry showed that

Fig. 1 X-ray diffraction patterns of the Ti-Cu alloys and titanium.

titanium and 5Cu alloy had an α -Ti phase, and that α -Ti and Ti_2Cu phases coexisted in the 10-20Cu alloys.

Microstructural composition images of the Ti-Cu alloys and titanium are shown in Fig. 2. As expected based on X-ray diffractometry results, acicular structures — which characterize α -Ti — appeared in the grains of titanium and 5Cu alloy. When Cu content increased to 10 mass%, a negligible amount of lamellae composed of α -Ti - Ti_2Cu could be found in the

matrix. Only one or two lamella structures were observed in the square area (10×10 mm) of 10Cu alloy. As the Cu content increased to 15 or 20 mass%, in addition to a large amount of lamellae in the grains, precipitates of Ti_2Cu were clearly observed in the grain boundaries.

Fig. 3 shows the anodic polarization curves of the Ti-Cu alloys and titanium. Fig. 3(a) shows that the passive region of all anodic polarization curves extended to 1.4 V, and that the values of their passive current density were the same in 0.9% NaCl solution. However, when the potential increased above 1.4 V and the alloys reached the transpassive region, the current density tended to increase as the Cu content of the alloys increased. Fig. 3(b) also shows the profiles of the anodic polarization curve in 1% lactic acid solution, which were similar to those in NaCl solution.

Fig. 4 shows the amount of ions released from the Ti-Cu alloys and titanium. As shown in Fig. 4(a), the amount of ions released from titanium was below the detection limit, and that Ti-Cu alloys released mainly Cu ions but hardly any Ti ions in 0.9% NaCl solution. Both 5Cu and 10Cu alloys released an average of $0.04 \mu\text{g}/\text{cm}^2$ Cu ions, and there were no significant differences in the amount of ions released from each alloy ($p > 0.05$). On the other hand, 15Cu and 20Cu alloys released significantly larger amounts of Cu ions than 5Cu and 10Cu alloys ($p < 0.05$). The amount of released Cu ions tended to be proportional to the Cu content of the Ti-Cu alloys in the 10-20 mass% range.

As shown in Fig. 4(b), titanium released an average of $2.3 \mu\text{g}/\text{cm}^2$ Ti ions, but the amount of Ti ions released from Ti-Cu alloys decreased to about 1.3-1.5 $\mu\text{g}/\text{cm}^2$ in 1% lactic acid solution. Regardless of the

Fig. 2 Composition images of the Ti-Cu alloys and titanium.

Fig. 3 Anodic polarization curves of the Ti-Cu alloys and titanium in 0.9% NaCl (a) and 1% lactic acid (b) solutions at 37°C.

Fig. 4 Amount of ions released from the Ti-Cu alloys and titanium in 0.9% NaCl (a) and 1% lactic acid (b) solutions at 37°C for 7 days.

Cu content, the amount of Ti ions released from the alloys showed no significant differences ($p > 0.05$). Although Cu ions were also released from the Ti-Cu alloys, the amount of released Cu ions was much smaller than the amount of released Ti ions ($p < 0.05$). 20Cu alloy released the largest amount of Cu ions, but it was less than 25% of the amount of Ti ions released from titanium. The amount of Cu ions released from 5Cu and 10Cu alloys were almost

equal ($p > 0.05$), but the amount released from 15Cu and 20Cu alloys were significantly larger than that from 5Cu and 10Cu alloys ($p < 0.05$). The amount of released Cu ions was nearly proportional to the Cu content of the Ti-Cu alloys in the same composition range of 10-20 mass% Cu.

DISCUSSION

Microstructural changes

According to the binary phase diagram of the Ti-Cu system²¹⁾, 5Cu alloy precipitates Ti₂Cu in α -Ti matrix through an eutectoid reaction in an equilibrium state. This is because little Cu can dissolve in a solid solution on the α -Ti side in a binary Ti-Cu alloy system at room temperature. Kikuchi *et al.*³⁾ noted that 5Cu alloy exhibited a typical hypoeutectoid structure which included primary precipitates of α -Ti and the eutectoid (lamellae of α -Ti and Ti₂Cu). However, they could not determine if Ti₂Cu existed in the 5Cu alloy using X-ray diffractometry – for even if Ti₂Cu existed, it would have been in a very small amount. Kaneko *et al.*²²⁾ indicated that there might be an intermediate phase in the hypoeutectoid region of binary Ti-Cu alloys which can precipitate during the eutectoid transformation from β -Ti to α -Ti and Ti₂Cu when the cooling rate is extremely rapid. They called this cooling rate “the critical cooling rate” in CCT diagrams.

5Cu alloy is believed to almost have the α -Ti phase coexist with a slight amount of an intermediate phase containing supersaturated Cu. Although a negligible amount of lamellae composed of α -Ti - Ti₂Cu was detected on the surface of 10Cu alloy, the surface area of Ti₂Cu on the alloy increased as the Cu content increased. Since Cu in excess of the solubility of α -Ti precipitates Ti₂Cu, the Cu content dissolved in α -Ti seemed to be constant regardless of the alloy composition beyond 5 mass% Cu.

Electrochemical stability

The passive region of all Ti-Cu alloys extended to 1.4 V, and their passive current densities were the same as that of titanium in NaCl or lactic acid solution, even when the surface area of Ti₂Cu grew larger as described above. Though the current densities in NaCl solution were slightly lower than those in lactic acid solution, the profiles of the anodic polarization curve in both solutions were almost the same. In terms of electrochemical oxidation under 1.4 V, there were no differences in the anodic polarization curve between titanium and the Ti-Cu alloys in either solution. In other words, α -Ti and Ti₂Cu composing the Ti-Cu alloys also showed the same corrosion resistance against electrochemical oxidation below 1.4 V.

Electrochemical oxidation above 1.4 V, however, moved the Ti-Cu alloys to the transpassive region and led to a gradual increase in their current density in both solutions as the surface area of Ti₂Cu grew larger. Current density depended solely on the area of Ti₂Cu because the Cu content of α -Ti coexisting with Ti₂Cu was constant and corresponded to the Cu solubility in the solid solution regardless of alloy composition, as described before. This phenomenon indicated that the dissolution rate of Ti₂Cu was

slightly higher than that of α -Ti in the transpassive region. Oda *et al.*⁶⁾ revealed that titanium alloyed with 5-50 at% Cu reduced the transpassive potential to 1.4 V, and that the precipitation of Ti₂Cu actually reduced corrosion resistance.

The difference between the dissolution rates of Ti₂Cu and α -Ti might be very slight. This was because Ti₂Cu on the surface did not dissolve preferentially in 0.9% NaCl solution after potentiostatic electrolysis was employed on 20Cu alloy at 1.7 V for two hours in 0.9% NaCl solution⁵⁾. In addition, Ti₂Cu and α -Ti maintained a low passive current density below 1.4 V, similar to that of titanium, although the current density of Ti-Cu alloys gradually increased in the transpassive region because of Ti₂Cu. These results explained why the electrochemical stability of Ti-Cu alloys, including α -Ti and Ti₂Cu, is superior to that of stainless steel and gold alloys used for dental appliances^{20,23)}.

Released ions

The amount of Cu ions released from 5Cu and 10Cu alloys were almost the same in either NaCl or lactic acid solution; statistical analysis showed no significant differences ($p > 0.05$). Since the microstructure of 5Cu alloy was nearly entirely composed of α -Ti and the microstructure of 10Cu alloy had a negligible amount of α -Ti - Ti₂Cu lamellae in the α -Ti matrix, the Ti₂Cu exposed on the surfaces of both alloys was little or extremely slight. Most probably, Cu ions were released mainly from α -Ti in both alloys. The Cu content dissolved in α -Ti was expected to be near the solubility in the solid solution and not to be totally different, because observable Ti₂Cu began to precipitate in the composition between 5-10 mass% Cu. In addition, as α -Ti released a small amount of Cu ions, there were no significant differences in the amount of Cu ions released from 5Cu and 10Cu alloys ($p > 0.05$). Therefore, it can be assumed that the average amount of Cu ions released from 5Cu and 10Cu alloys was the same as that released from α -Ti in each Ti-Cu alloy.

On the other hand, as the Cu content of the Ti-Cu alloys increased to 15 or 20 mass%, the Ti₂Cu exposed on the surface of the alloys also increased. The increase in the surface area of Ti₂Cu led to a proportionality relation between the amount of released Cu ions and the Cu content of the alloys in the range of 10-20 mass%. Then, when the correlation between the amount of released Cu ions and the Cu content in the 10-20 mass% range was calculated, Equations (1) and (2) were obtained for the NaCl and lactic acid solutions respectively, as shown below.

$$W_{\text{Cu elution}} = 0.0072 \times [\text{Cu}] - 0.0278 \quad (r = 0.965) \quad (1)$$

$$W_{\text{Cu elution}} = 0.0295 \times [\text{Cu}] - 0.1769 \quad (r = 0.937) \quad (2)$$

Here, $W_{\text{Cu elution}}$, $[\text{Cu}]$, and r represent the amount of released Cu ions ($\mu\text{g}/\text{cm}^2/7$ days), Cu

content (mass%) of Ti-Cu alloy, and correlation coefficient respectively. Since both correlation coefficients were close to 1, each function between the amount of released Cu ions and Cu content (in NaCl and lactic acid solutions) matched well the approximation of linear expression.

The amount of Cu ions released from Ti₂Cu in NaCl and lactic acid solutions can be obtained from Equations (1) and (2) respectively. When $W_{\text{Cu from } \alpha}$ and $W_{\text{Cu from Ti}_2\text{Cu}}$ represent the amount of Cu ions released from α -Ti and Ti₂Cu respectively, $W_{\text{Cu elution}}$ can be represented by Equation (3).

$$W_{\text{Cu elution}} = W_{\text{Cu from } \alpha} + W_{\text{Cu from Ti}_2\text{Cu}} \quad (3)$$

When Equation (3) is rearranged, Equation (4) is obtained as follows:

$$W_{\text{Cu from Ti}_2\text{Cu}} = W_{\text{Cu elution}} - W_{\text{Cu from } \alpha} \quad (4)$$

As mentioned before, there were no significant differences in the amount of Cu ions released from 5Cu and 10Cu alloys. If the Cu content dissolved in α -Ti reached the solubility limit in the solid solution, $W_{\text{Cu from } \alpha}$ can be equal to the average amount of Cu ions released from 5Cu and 10Cu alloys (0.0379 ± 0.0041 ($\mu\text{g}/\text{cm}^2/7$ days) and 0.0962 ± 0.0327 ($\mu\text{g}/\text{cm}^2/7$ days) in the NaCl and lactic acid solutions respectively).

The amount of Cu ions released from α -Ti was very small in both solutions. When Equations (1) and (2) are substituted for Equation (4), Equations (5) and (6) are obtained respectively as follows.

$$W_{\text{Cu from Ti}_2\text{Cu}} = 0.0072 \times [\text{Cu}] - 0.0278 - W_{\text{Cu from } \alpha} \quad (5)$$

$$W_{\text{Cu from Ti}_2\text{Cu}} = 0.0295 \times [\text{Cu}] - 0.1769 - W_{\text{Cu from } \alpha} \quad (6)$$

If a Ti-Cu alloy has a single phase of Ti₂Cu, a Cu content of 40 mass% can be obtained from the binary phase diagram of the Ti-Cu system²¹⁾. Then, $W_{\text{Cu from Ti}_2\text{Cu}}$ becomes 0 because α -Ti disappears in the Ti-Cu alloy containing 40 mass% Cu. When the Cu content of 40 mass% and $W_{\text{Cu from Ti}_2\text{Cu}} = 0$ were substituted for Equations (5) and (6), the amount of Cu ions released from Ti₂Cu in the NaCl and lactic acid solutions were 0.260 ($\mu\text{g}/\text{cm}^2/7$ days) and 1.003 ($\mu\text{g}/\text{cm}^2/7$ days) respectively. Although the amount of Cu ions released from Ti₂Cu was larger than that from α -Ti in both solutions, the amount released from Ti₂Cu in the NaCl solution was 1/10 times smaller than that from type 4 gold alloy under the same conditions. Even the amount of Cu ions released from Ti₂Cu in the lactic acid solution, which was four times larger than that released in the NaCl solution, was almost the same as that from type 4 gold alloy in the same solution²⁴⁾.

A series of Ti-Cu alloys also released Ti ions in the lactic acid solution, but alloying with Cu significantly ($p < 0.05$) reduced the amount of Ti ions released from titanium. The Ti ions seemed to be released mainly from α -Ti in the Ti-Cu alloys because

the amount of Ti ions released from 5Cu-20Cu alloys was statistically the same ($p > 0.05$) even when the precipitation of Ti₂Cu increased. This speculation was based on area of α -Ti that hardly changed in the range of 5Cu-20Cu alloys, since the area of Ti₂Cu exposed on the surface was much smaller than that of α -Ti.

Although Ti₂Cu is an intermetallic compound, the preferential dissolution or elution of a large amount of Cu ions is worrisome. The findings in this study gave proof that Ti₂Cu released a small amount of Cu ions and maintained a stability similar to that of titanium against electrochemical oxidation under 1.4 V. However, even though the series of Ti-Cu alloys with α -Ti or α -Ti and Ti₂Cu examined in this study showed excellent performance in the light of both ion elution and electrochemical stability, the amount of released ions should be as small as possible. Therefore, if effects of Ti₂Cu on grindability, machinability, and mechanical properties are applied to titanium alloys, it is desirable to achieve these improvements by using a minimum amount of Ti₂Cu since Ti₂Cu released a slightly higher amount of Cu ions than α -Ti.

CONCLUSION

Ti-Cu alloys containing 5-20 mass% Cu showed anodic polarization curves similar to that of titanium at electrochemical oxidation below 1.4 V in 0.9% NaCl and 1% lactic acid solutions. However, their current densities tended to increase in the transpassive region above 1.4 V as the Cu content of the alloys increased. Although the precipitation of Ti₂Cu mainly induced an increase in current density, the increase was small and the anodic polarization curve did not appear to break down. These results indicated that α -Ti or Ti₂Cu composing Ti-Cu alloys had good stability against electrochemical oxidation.

A correlation between the released Cu ions and the Cu content of the alloys gave the amount of Cu ions released from Ti₂Cu. Values of 0.260 and 1.003 ($\mu\text{g}/\text{cm}^2/7$ days) in NaCl and lactic acid solutions, respectively, were obtained. Although these values were larger than those from α -Ti, they were not more than those from type 4 gold alloy. Therefore, α -Ti and Ti₂Cu composing the Ti-Cu alloys apparently have sufficient corrosion resistance for use as dental alloys with respect to their electrochemical stability and elution of ions.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Sumitomo Titanium Corporation for providing high-purity titanium sponges, as well as the members of the Industrial Technology Institute, Miyagi Prefectural Government, for their kind cooperation in the ion analyses.

REFERENCES

- 1) Okuno O, Shimizu A, Miura I. Fundamental study on titanium alloys for dental casting. *J J Dent Mater* 1985; 4: 708-715.
- 2) Takahashi M, Kikuchi M, Takada Y, Okuno O. Mechanical properties and microstructures of dental cast Ti-Ag and Ti-Cu alloys. *Dent Mater J* 2002; 21: 270-280.
- 3) Kikuchi M, Takada Y, Kiyosue S, Yoda M, Woldu M, Cai Z, Okuno O, Okabe T. Mechanical properties and microstructures of cast Ti-Cu alloys. *Dent Mater* 2003; 19: 174-181.
- 4) Kikuchi M, Takahashi M, Okuno O. Mechanical properties and grindability of dental cast Ti-Nb alloys. *Dent Mater J* 2003; 22: 328-342.
- 5) Takada Y, Nakajima N, Okuno O, Okabe T. Microstructure and corrosion behavior of binary titanium alloys with beta-stabilizing elements. *Dent Mater J* 2001; 20: 34-52.
- 6) Oda Y, Funasaka M, Sumi T. Corrosion of dental titanium alloys – Binary system of Ti-Al, Ti-Cu, Ti-Ni. *J J Dent Mater* 1990; 9: 314-319.
- 7) Takahashi M, Kikuchi M, Takada Y, Okuno O, Okabe T. Corrosion behavior and microstructures of experimental Ti-Au alloys. *Dent Mater J* 2004; 23: 109-116.
- 8) Watanabe K, Miyakawa O, Takada Y, Okuno O, Okabe T. Casting behavior of titanium alloys in a centrifugal casting machine. *Biomater* 2003; 24: 1737-1743.
- 9) Shimizu A. Studies on titanium alloys for dental casting Part I: Effects of Pd and Cr on titanium properties. *J J Dent Mater* 1986; 5: 122-132.
- 10) Okuno O, Hanmanaka H. Application of beta titanium alloys in dentistry. *Dentistry in Japan* 1989; 26: 101-104.
- 11) Takemoto S, Hattori M, Yoshinari M, Kawada E, Asami K, Oda Y. Corrosion behavior and surface characterization of Ti-20Cr alloy in a solution containing fluoride. *Dent Mater J* 2004; 23: 379-386.
- 12) Takahashi M, Kikuchi M, Okuno O. Mechanical properties and grindability of experimental Ti-Au alloy. *Dent Mater J* 2004; 23: 203-210.
- 13) Kikuchi M, Takada Y, Kiyosue S, Yoda M, Woldu M, Cai Z, Okuno O, Okabe T. Grindability of cast Ti-Cu alloys. *Dent Mater* 2003; 19: 375-381.
- 14) Shimizu H, Habu T, Takada Y, Watanabe K, Okuno O, Okabe T. Mold filling of titanium alloys in two different wedge-shaped molds. *Biomater* 2002; 23: 2275-2281.
- 15) Kikuchi M, Takahashi M, Okabe T, Okuno O. Grindability of dental cast Ti-Ag and Ti-Cu alloys. *Dent Mater J* 2003; 22: 191-205.
- 16) Yoneyama T, Doi H, Hamanaka H. Ion releasing from base-metallic biomaterials. Report of the Institute for Medical & Dental Engineering 1992; 26: 9-13.
- 17) Yoneyama T, Doi H, Hamanaka H. Released metallic ions from Ti, Ti-6Al-4V alloy and Ni-Ti alloy. *Seitaizairyo* 1993; 11: 71-78.
- 18) ASM International Handbook Committee. Corrosion: Fundamentals, testing, and protection. ASM handbook volume 13A, 1st ed, ASM International, Metals Park, Ohio, 2003, pp.266-268.
- 19) Warren D. The effect of sigma phase vs. chromium carbides on the intergranular corrosion of type 316 and 316L stainless steel. *Corrosion* 1958; 15: 213-232.
- 20) Takada Y. Corrosion resistance of dental alloys evaluated from released ions. *Corrosion Engineering* 2000; 49: 669-685.
- 21) ASM International Committee. Phase diagrams of binary titanium alloys. Monograph series on binary alloy phase diagrams, 2nd ed, ASM International, Metals Park, Ohio, 1990, pp.80-95.
- 22) Kaneko H, Huang YC. Continuous cooling transformation characteristics of titanium alloys of eutectoidal type (Part 2). *J Japan Inst Metals* 1963; 27: 398-402.
- 23) Takada Y, Okuno O. Corrosion behavior of stainless steels and dental precious alloys used for dental magnetic attachments. *J J Mag Dent* 1994; 3: 14-22.
- 24) Takada Y, Ito M, Kimura K, Okuno O. Electrochemical properties and released ions of Au-1.6mass%Ti alloy. *Dent Mater J* 2005; 24: 153-162.