bonded to identically shaped acrylic brackets (data not shown). Despite great efforts, we have been unable to correlate these results with any specific material property. However, there might be possibility that tooth + zirconia bracket mimics the ceramic capacitor [25,26]. When the capacitors are electrified, magnetic fields are generated around them [27]. These generated magnetic fields could induce the electric current, and might amplified the current level in tooth. It is likely that unexpected rank order of induced current is due to combination of tooth and material properties of the appliance components other than their materials and resistivity themselves.

In this study, we have shown that the low-frequency magnetic fields induced by electric toothbrushes and light curing units induce electric current in tooth tissue, irrespective of whether these teeth are bonded to SUS or ZrO_2 brackets. We have also shown that thermal effects of the curing lights to tooth surface could not be due to their magnetic field-induced current in teeth, and ceramic appliances combined with teeth mimic capacitors when exposed to magnetic fields. It is very difficult to protect ourselves from low-frequency magnetic fields as they can pass through human tissue and most other materials, including glass, plastic, metals and concrete [19]. The only viable way to limit exposure to low-frequency electromagnetic fields is thought to be elimination of their generation by electrical home appliances and dental devices. We conclude that the currents generated in teeth by these devices is significant, and that further study is necessary to clarify exactly how they impact on human oral health and whether countermeasures can be developed to negate their effects.

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Ⅲ．研究成果の刊行に関する資料⑤

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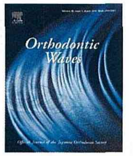

Research paper

Modification of metallic materials for a white appearance without coating and plating

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ABSTRACT

Purpose: The purpose of this study was to develop white-colored metals for metal injection moldings, and white-colored surface preparation for metals to satisfy the esthetic demands of patients.

Materials and methods: Two methods for white coloration of metals were developed for two kinds of metals. For white-colored silver metal, silver powder was baked at 700 °C for 15 min with or without the alumina plate. For white-colored surface preparation, titanium wire, orthodontic brackets and dental implants were baked at 1000 °C for 15 min. Two kinds of white-colored specimens were used for evaluation of coloration, mechanical strength and the components.

Results: Treated silver metal was visually white, and closed to the color of white porcelain panel evaluated by a colorimeter. From the results of load-deflection tests, the mechanical strength of white-colored silver metal was almost same as that of non-treated one. Surface prepared titanium objects were also visually white, and closed to the color of white porcelain, and thickness of white color layer was 10–50 μm. Load-deflection tests revealed that white-colored titanium metal was fragile compared to non-treated one. The component of white-colored silver metal was approximately 100% Ag. On the other side, the surface component of white-colored titanium metal was titanium dioxide.

Conclusion: Two methods of white coloration for metals were developed. One method is use of injection molding especially for prevention of crushing of ceramics when combined with them. The other is a white-colored surface preparation for dental appliances, including orthodontic appliances.

1. Introduction

When the metal is transformed, the atomic bond is maintained by free electrons even if the position of the atomic bond is changed. This is why metals can be changed and processed without breaking by application of external forces, in contrast to the easy breaking of ceramics by relatively small forces. The metal surface of free electrons reflects all visible wavelengths and maintains its silver metallic luster [1,2]. Because of their toughness, metals were widely used in many fields, including the clinical dental field. Recently, patients have tended to demand that more attention be paid to the appearance of dental materials as well as their satisfactory performance, which has led to dental materials being based on white-colored materials, i.e. plastic resins and ceramics. However, they do not possess the toughness associated with metals. Ceramics are easy to break by application of external forces, i.e. biting forces, and could not be readily bent because of their brittleness [2]. Plastic resins could be bent a little; however, this quality was easily affected by degradation in the oral environment [2]. This contradiction between patient demands and the physical properties of dental materials could be resolved if we could make bendable ceramics, non-degradable plastic resins or white-colored metals. Literature search of the word "white" and "metal/alloy" revealed some papers [3,4]. Anodic oxidation of titanium makes titanium dioxide on the surface of that for improvement of corrosion resistance, and could color the titanium [5–8]. However, metallic luster of titanium could not be diminished [8]. Therefore, we developed two methods of making white-colored metal without coating and plating for compatible, both excellent mechanical characteristics and esthetics as orthodontic appliances. One method is for injection moldings especially for prevention of crushing of ceramics when combined with them. This led us make non-crushing ceramic orthodontic appliances and metal bonded crowns in a rapid manner, i.e. making tooth-colored crowns/bridges during chair-time or on the day of the first medical examination (patent pending). The other method concerns white-colored surface preparation for titanium dental appliances, including orthodontic appliances (patent pending). In this paper we show the methods of making white-colored metals without any plating and coating.

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2. Materials and methods

2.1. Materials

Preliminary experiments for making "white-colored metal" were carried out using various kinds of metals by a range of methods. The color of metal was judged by visual observations in these screening experiments. From the results of these experiments, it was possible that silver and titanium could be rendered white-colored without any coating and plating, so that silver powder (Ag-HWQ 2.5 μm, Fukuda Metal Foil & Powder Co. Ltd., Kyoto, Japan), and ingots (10 mm φ × 15 mm) or 1 mm thickness discs of titanium (T-Alloy M, GC Co. Ltd., Tokyo, Japan) were used for these experiments. Discs of titanium were prepared by cutting ingots with a diamond disc saw (Isomet low speed saw model no. 11-1280-170 with Buehler wafering blades, Buehler Inc., IL, USA). We considered using silver as a lining metal in ceramic dental appliances to prevent breaking in the oral environment, because silver powder could be used like silver clay as a filling material. Therefore, we used not only silver itself for the white-colored metal, but also baked on alumina ceramic plates (Asuzac Co. Ltd., Nagano, Japan). Titanium was used as a white-colored metal by white-colored surface preparation for dental appliances.

2.2. *Representation of objects made of white-colored metal by injection molding, and prepared by white surface coloring*

To represent the white-colored objects, we made a white-colored metal bonded crown by molding using silver powder. A zirconia crown was milled using a CAD/CAM milling machine (Cadim, Advance Co. Ltd., Tokyo, Japan). The zirconia crown was then filled by gray-color silver powder mixed with hydrogen peroxide solution, and pressed onto an artificial tooth prepared by using a cutting tool with a diamond point. After removal of surplus silver clay, the material was baked at 700 °C for 15 min in a furnace (KDF009G, Denken Co. Ltd., Kyoto, Japan). For objects with white-colored surface preparation, we used orthodontic brackets (Rematitan titanium bracket, Dentaurum, Ispringen, Germany) and one piece type dental implants (μ-one, Yamahachi Dental Mfg. Co., Aichi, Japan) made of pure titanium. They were baked at 1000 °C for 15 min in a furnace for white color preparation.

2.3. *Measurement of color*

To measure the color of white-colored metal discs (silver; 10 mm × 10 mm × 2 mm, baked at 700 °C for 15 min, titanium; 10 mm φ × 1 mm, 1000 °C for 15 min), we used a colorimeter (CR-100, Minolta Co. Ltd., Tokyo, Japan). The colorimeter was calibrated by the standard white porcelain plate, an accessory of the instrument, before estimation of the color value of the samples. We also estimated the color of intact silver and titanium plate compared to white-colored metals.

We measured L^* (lightness of color, $L^* = 0$ yields black and $L^* = 100$ indicates diffuse white), a^* (position between red/magenta and green, negative values indicate green while positive values indicate magenta) and b^* (position between yellow and blue, negative values indicate blue and positive values indicate yellow) and calculated ΔE^*ab (ΔE) using CIELAB [9,10]. Color differences between white porcelain plate and intact metal/white-colored metal were exhibited as ΔE, which was calculated by the following equation:

$$\Delta E * ab = [(\Delta L*)2 + (\Delta a*)2 + (\Delta b*)2]^{1/2}$$

The color difference value (ΔE) was defined by the NBS unit (National Bureau of Standards, National Institute of Standards and Technology, MD, USA) as follows: 0–0.5; trace, 0.5–1.5; slight, 1.5–3.0; noticeable, 3.0–6.0; appreciable, 6.0–12.0; much, 12.0–; Very much. Comparing the value of ΔE of intact metal and white-colored metal, we could establish whether the color of white-colored metals was close to that of white porcelain plate.

2.4. *Thickness of white color layer on the titanium surface*

To estimate the thickness of white color layer of titanium surfaces, dental implants were used, because they contained two different polished surfaces (mirror polished and sand blasted surfaces) and screw shaped part. First, white color-treated dental implant was embedded in acrylic resin using embedding machine (PNEUMET II mounting press, Buehler Inc., IL, USA). After embedding, specimen was cut longitudinally by a diamond disc saw. Observation and thickness estimation of white color layer of the dental implant was performed with a metallurgical microscope (BX51, Olympus Co., Tokyo, Japan). Observation and estimating point of cross section of the dental implant was three points, i.e. mirror polished abutment part, sand blasting of the deepest part of the screw thread of fixture part, and sand blasting of the top part of the screw thread of fixture part.

2.5. *Three-point bending tests and mechanical characteristics*

To confirm the flexibility, especially the bending ability of the white-colored metal, we performed three-point bending tests using a universal testing machine (AG-I, Shimadzu Co. Ltd., Kyoto, Japan) with 20 mm support span. For this experiment, intact and white-colored metals were prepared, i.e. silver plates (metal colored one and white one which baked at 700 °C for 15 min after mixture of silver powder and distilled water, 5 mm × 5 mm × 35 mm) and titanium wires (one untreated one and one white surface prepared by baking at 1000 °C for 15 min, 1 mm φ × 35 mm) as test pieces. Cast and mold of titanium was difficult, and silver plates could not be made in the same size as titanium wires, because of their low strength, and shrinking and deformation during baking. This is the reason why silver and titanium specimens were of different size.

Moreover, samples combined with intact/white-colored metal and ceramics were also prepared. Silver clay was coated onto an alumina ceramic plate (3 mm × 0.5 mm × 50 mm) with 1 mm thickness using a mixture of silver powder and distilled water or hydrogen peroxide solution (approximately 30% hydrogen peroxide solution, Wako Co. Ltd.), and then they were baked at 700 °C for 15 min in a furnace. This thickness of silver metal on alumina plate was decided considering the clearances between abutment tooth and opposing tooth, and thickness of parts of ceramic made orthodontic appliances.

To investigate the mechanical characteristics of white-colored silver metal, plates were prepared (5 mm × 5 mm × 35 mm, baked at 700 °C for 15 min). We calculated the coefficient of volume contraction, porosity and bending strength by means of the following equations [2]:

(A) Volume contraction (%)

$$\left[\frac{\text{volume before baking} - \text{volume after baking}}{\text{volume before baking}}\right] \times 100$$

(B) Porosity (%)

$$\left[\frac{\text{Density}^{*}\text{ of silver}(=10.5) - \dfrac{\text{density of porous}}{\text{white-cloured metal}}}{\text{Density of silver}}\right] \times 100$$

*Density (g/cm^3) = weight after baking/volume after baking.

(C) Bending strength (MPa) $\frac{3\times\text{maximum load}\times\text{support span}}{2\times\text{width of sample}\times\text{height of sample}^2}$.

2.6. *Component analysis by electron probe microanalysis and laser Raman spectrometry*

We performed component analysis of the white-colored silver metal and white-colored surface preparation of titanium metal using an electron probe microanalyzer (EPMA; JXA-8100, JEOL Co. LTD., Tokyo, Japan) [11]. For this analysis, we prepared silver discs (a metal colored one and white one which baked at 700 °C for 15 min, 10 mm × 10 mm × 2 mm) and titanium ingots (non-treated one and white-colored surface prepared one which baked at 1000 °C for 15 min, 10 mm φ × 15 mm) as test pieces. To investigate the oxide on the surface of the titanium disc, Raman spectroscopy was performed to clarify whether titanium oxide on the disc was rutile or anatase using a laser Raman spectrometer (NRS-3100, JASCO Co. Ltd., Tokyo, Japan) [12]. For this analysis, we prepared the white-colored surface prepared titanium ingots (10 mm φ × 15 mm, baked at 1000 °C for 15 min) as a test piece. These analyses were performed at the Industrial Research Institute of the Niigata Prefecture as a trusted third party. Each analysis was conducted according to the standard protocol [13].

2.7. *Data and statistical analysis*

From the data of each experiment 8 out of 10 data points were obtained, which meant that the maximum and minimum data were removed. These 8 data were calculated and represented as means ± standard deviations. The statistical significance of differences between group means was determined by means of a t-test.

3. Results

3.1. *Representation of objects made of white-colored metal by injection molding, and prepared by white-colored surface preparation*

We tried to make white color metals and/or white-colored surface preparation for metals by many methods and materials, and found that silver metal and titanium metal could be changed from metallic color to white.

Silver metal exhibited a white color by injection molding using silver clay consisting of silver powder and binder (solution) (Fig. 1A and 2). This phenomena could be found when silver clay was baked at 650–720 °C for 10–20 min We thus decided that the experimental condition was baking of silver clay at 700 °C for 15 min.

Titanium metal could exhibit a white color as a result of surface heat treatment (Fig. 1B and C). To clarify the heat condition for the white-colored treatment of titanium, we first examined the experimental conditions. Appropriate conditions for white treatment were 1000 °C for 5–15 min and 1100 °C for 2.5–5 min (Fig. 3). In the case of insufficient heating conditions, the surface of titanium exhibited a gray color. In contrast, excess heating turned the titanium surface yellow and also resulting in peeling. From this results, we decided that the experimental condition was baking of titanium at 1000 °C for 15 min White color treatment of titanium products are represented in Fig. 4.

3.2. *Measurement of color differences*

We estimated the color of white-colored metals by the colorimeter. In silver metals, the colors were close to that of

Fig. 1 – Representation of white-colored metal. (A, left) metal-colored silver plate; right: white-colored silver plate made from silver clay for filling materials. White bar indicates 1 cm (B, left) an intact titanium ingot; right: white color-prepared titanium ingot. White bar indicates 5 mm, and (C) high magnification of "C" (10×). Black bar indicates 1 mm

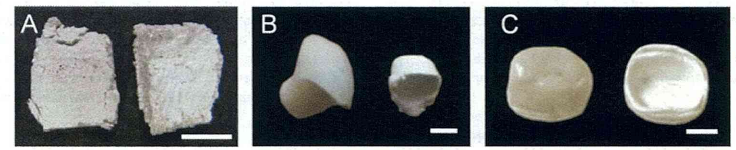

Fig. 2 – White-colored silver metal and metal-supported zirconia crown. (A) Mass of baked silver clay. Left: white-colored solid sample; right: white-colored foamed sample, (B) white solid metal-supported crown, and (C) a crown supported by white foamed metal made from silver clay with 30% hydrogen peroxide.

the standard white porcelain panel, whereas, metallic colored silver was not close to this value (Table 1A).

In titanium metals, values of color differences (ΔE) of white color-treated titanium metals were close to the standard porcelain panel compared to intact titanium metals (Table 1B).

3.3. *Three-point bending tests of white-colored metals*

The bending strength of white silver was almost same as that of the metallic one in the elastic region, however, the bending strength of the white sample was lower than that of the metallic one in the plastic region (Fig. 5A).

For titanium, the bending strength of the white sample was almost identical to that of the metallic one in the elastic region. In the plastic region of bending strength the white titanium was increased, but fragile compared to the metallic titanium specimen (Fig. 5B).

3.4. *White silver metals for injection molding*

We considered using white-colored metals for injection molding as the materials for orthodontic appliances, but found that silver was too low in strength for this application. For this reason, we decided to use them for prevention of

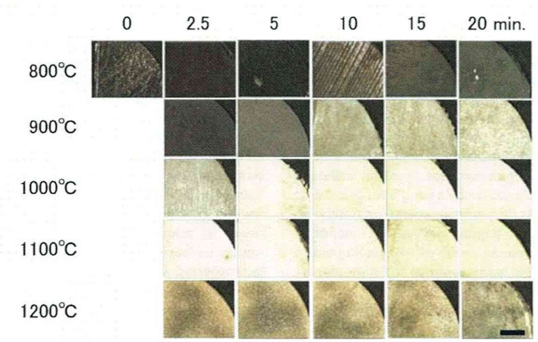

Fig. 3 – Baking conditions for making white-color prepared titanium metal. Black bar indicates 2 mm

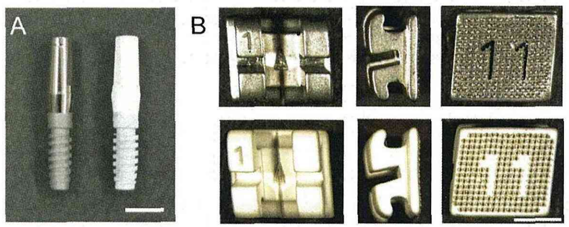

Fig. 4 – White color preparation for dental implants and orthodontic brackets. (A) Dental implants. Left: non treatment; right: white color treatment. White bar indicates 5 mm (B) orthodontic brackets upper: non-treatment, lower: white color treatment. White bar indicates 2 mm

Table 1 – Color differences (ΔE) between intact and white colored-metals.

	L^*	a^*	b^*	ΔE^*ab
A. Silver metal				
Standard white porcelain panel	97.88 ± 0.18	0.42 ± 0.00	−0.38 ± 0.00	
Silver	70.92 ± 0.74	0.32 ± 0.00	−0.28 ± 0.00	26.97 ± 0.74
White-colored silver metal	95.92 ± 0.53	0.41 ± 0.00	−0.36 ± 0.00	1.97 ± 0.53
B. Titanium metal				
Standard white porcelain panel	97.9 ± 0.1	0.40 ± 0.00	−0.37 ± 0.06	
Titanium	62.4 ± 4.1	1.00 ± 0.26	3.67 ± 1.10	35.8 ± 4.3
White-color prepared titanium metal	78.9 ± 1.7	−0.70 ± 0.46	4.47 ± 0.42	19.6 ± 1.6

$n = 8$.

crushing of the ceramic orthodontic appliances by lining of white colored metals. For this experiment, we used ceramic crown caps with white colored metal lining. First, solid silver clay was used for lining of CAD/CAM-made ceramic crown caps, but the cap and white-colored metal liner were found to have separated after baking by shrinkage of the white-colored metal (Fig. 2B). We tried to suppress the shrinkage of the silver clay by baking with porosity, using hydrogen peroxide solution (Fig. 2A and C). After baking ceramics with porous silver clay, they attached strongly (Fig. 2C and 6).

In this step, we needed to investigate appropriate concentration of hydrogen peroxide for silver clay and the effects of porosity on the characteristics of white silver metal. Surface and color differences of porous white silver are represented in Fig. 7 and Table 2, respectively. Then we examined the mechanical characteristics of porous white silver (Fig. 8). From these results, silver clay with 3% of H_2O_2 exhibited the highest porosity and was the weakest in terms of mechanical strength. In contrast, silver clay with 30% of H_2O_2 exhibited the lowest porosity and highest mechanical strength with low shrinkage

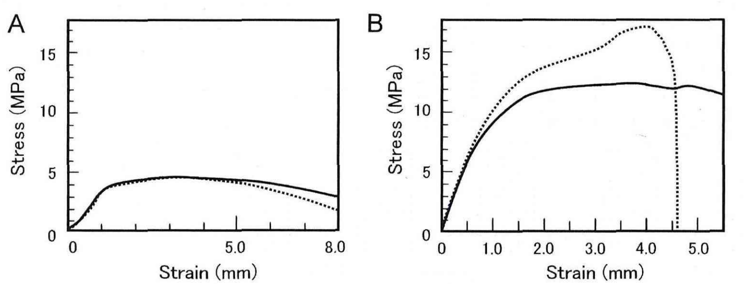

Fig. 5 – Stress–strain curves of white-colored metals. (A) silver metal (5 mm × 5 mm × 35 mm), (B) titanium metal (1 mm φ × 35 mm). Solid lines indicate the results of conventional metals, and dotted lines indicated those of white colored metals. Support spans were 20 mm

Fig. 6 – Detached white-colored silver metal heated at 700 °C on zirconia plate. Left: solid metal; right: porous metal made from silver clay with 30% hydrogen peroxide. Solid metal could detached from ziriconia plate easily (A), however, strong force was needed to detach the porous one from zirionia plate with remaining of porous one (B). Black bar indicates 1 cm

during baking (Fig. 8). Silver clay with distilled water (0% of H_2O_2) exhibited 7–8% of porosity.

Next, we estimated the mechanical strength of a combination of ceramics and white silver metals (Figs. 9 and 10). The lining of silver metal to the alumina ceramic plate increased the breaking point (Fig. 9A). In addition, the resilience of the combination of ceramics and metal exhibited a high value compared with that of the ceramic alone (Fig. 9B). Lining of porous metals to ceramics led to strengthened mechanical characteristics compared with the lining of non-porous samples (Fig. 9).

From the observation of testing samples after breaking, porous metals still adhered to the ceramic plates, whereas non-foamed metals had become detached in the region of alumina fracture point and 5 mm from that point. (Fig. 10A and B). After white-colored silver metal heated at 700 °C on zirconia plate, solid metal could detached from ziriconia plate easily, however, strong force was needed to peel the porous metal from zirونia plate with remaining of porous one, which exhibited white color (Fig. 6).

3.5. *White color treatment for titanium metals and thickness of their white color layer*

We tried to make titanium dental products, i.e. dental implants and orthodontic brackets with a white color by this method and found that both of them exhibited a white color (Fig. 4A and B). This method changed only the surface of titanium and we estimated the vertical slot sizes of metallic and white color brackets. Both bracket slot sizes were almost same and exhibited no statistically significant differences (Table 3).

We evaluate the thickness of white color layer in cross section of dental implant at three points, i.e. mirror polished abutment part, sand blasting of the deepest part of the screw thread of fixture part, and sand blasting of the top part of the screw thread of fixture part (Fig. 11A). About mirror polished abutment part of dental implant, thickness of white color layer was 40.0–53.3 μm (average ± SD; 44.5 ± 5.6 μm) (Fig. 11B and Table 4). Sand blasting of the deepest and top part of the screw thread of fixture part was exhibited 10.7–16.0 μm (average ± SD; 13.9 ± 2.2 μm) and 26.7–36.0 μm (average ± SD; 31.7 ± 3.7 μm), respectively (Fig. 11C and D; Table 4). Rank order of thickness of white color layer on the dental implant was mirror polished abutment part > sand blasting of the top

Table 2 – Color differences (ΔE) between foamed and non-foamed white colored silver generated from silver clay with 30% hydrogen peroxide.

	L^*	a^*	b^*	ΔE^*ab
Standard white porcelain panel	97.78 ± 0.57	0.42 ± 0.01	−0.37 ± 0.01	
Silver	70.92 ± 0.74	0.32 ± 0.01	−0.29 ± 0.01	26.87 ± 0.74
White-colored silver metal	95.93 ± 0.55	0.41 ± 0.01	−0.36 ± 0.01	1.85 ± 0.55
White-colored foamed silver metal	90.95 ± 1.15	0.36 ± 0.02	−0.36 ± 0.01	6.83 ± 1.15

$n = 8$.

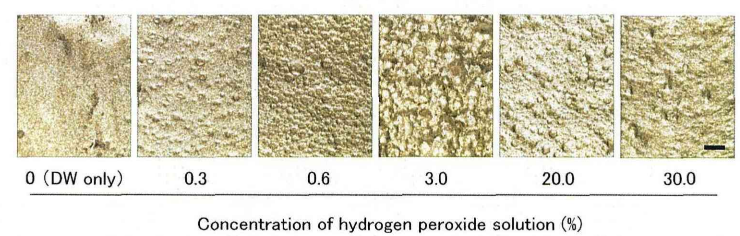

Fig. 7 – Surface of white-colored silver metal made from silver clay with various concentrations of hydrogen peroxide (20×). Black bar indicates 0.5 mm

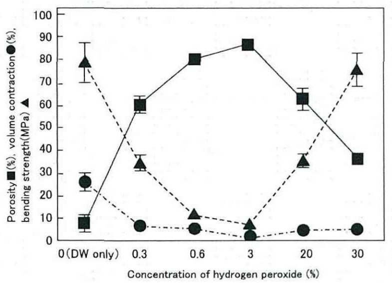

Fig. 8 – Effects of concentration of solution for increase of porosity (H_2O_2) on mechanical characteristics of white-colored silver metal.

part of the screw thread of fixture part > sand blasting of the deepest part of the screw thread of fixture part. White color layer covered all titanium surface of the dental implant (Fig. 11)

3.6. *Component analysis by electron probe microanalysis and laser Raman spectrometry*

To clarify the causes of this white color of metals, we performed component analysis using an electron probe microanalyzer. For silver metals, surface conditions were quite different between metallic (baked silver clay at 900 °C for 15 min) and white-colored ones (baked silver clay at 700 °C for 15 min) from scanning electron micrographs (1000×) (Fig. 12A–C). In white-colored silver groups, no significant differences in scanning electron micrographs between solid and porous ones could be observed (Fig. 12 B and C). However, components of them were almost same, i.e. more than 98 mass% and 93 at% of them were silver (Table 5).

In titanium metals, surface conditions were also different between metallic and white color samples as seen from scanning electron micrographs (1000×) (Fig. 13A and B). In white color sample, scanning electron micrographs revealed oxides covered the titanium surface (Fig. 13B). From the component analysis, the white color of the titanium surface was due to titanium dioxide (Table 6). We then examined the type of this titanium dioxide by a laser Raman spectroscopy, which revealed that white-colored surface was rutile type titanium dioxide (Fig. 14).

4. Discussion

Recently there has been a growing tendency of patients to demand that dental treatments involve an acceptable appearance as well as sound dental properties. However, the metal surface of free electrons reflects all visible spectra and it keeps its silver metallic luster. This property is due to the metallic bond [1,2]. When the metal is transformed, the atomic bond is maintained by free electrons even if the position of the atomic bond is changed, so that metals can be changed and processed without breakage and widely used in dental field [1,2]. This contradiction between patients' demands and physical properties of dental materials could be resolved by the making of bendable ceramics, non-degradable plastic resins or white-colored metals. There are some papers whose titles include the word "white" and "metal/alloy" [3,4]. Anodic oxidation of titanium could also color the titanium [8]. However, their "white" is not white but silver metallic luster observed by the naked eye. Therefore, we developed two methods of making white-colored metal without coating and plating as described in this paper. From our trial to make white-colored metals and/or white-colored surface preparations for metals by many methods and materials, silver and titanium metal were found to change their metallic color to white.

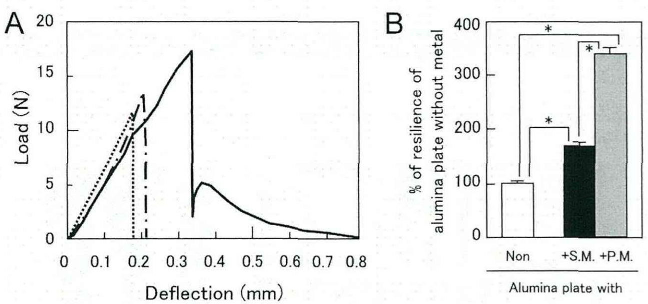

Fig. 9 – Mechanical characteristics of alumina ceramic plate lining with white-colored silver metal. (A) Load-deflection curve. Dotted line; alumina plate (0.5 mm thickness), semi-dotted line: alumina ceramic plate (0.5 mm thickness) with solid silver (1.0 mm thickness), solid line; alumina ceramic plate (0.5 mm thickness) with porous silver (1.0 mm thickness). (B) Resilience of alumina ceramic plate lining with or without white-colored metal. S.M., solid silver; P.M., porous silver. *P < 0.01, statistical analysis by t-test.

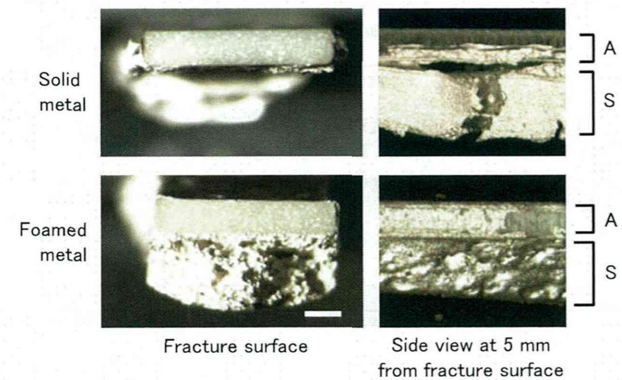

Fig. 10 – Conditions of testing samples after three-point bending tests. (A) alumina plate, (S) silver metal. White bar indicates 1 mm

Silver metal exhibited white color after baking a silver clay comprising silver powder and binder solution. We considered using white color metals for injection molding as the materials for orthodontic appliances, i.e. brackets and molar tubes, but found that silver metal was too low in strength for such applications. For this reason, we elected to use them for prevention of crushing in ceramic appliances and metal-bonded crowns lining the ceramic crown caps. However, white-colored metal became detached from the ceramic plates during the baking process, because of their high shrinkage (Fig. 2B). Thus we selected creation of porous metals in order to decrease this shrinkage, using hydrogen peroxide. Appropriate concentration of hydrogen peroxide for silver clay was investigated and it was found that a suitable concentration was 30%. The concentration of undiluted solutions of hydrogen peroxide on the market was approximately 30%. To examine the effects of porosity on the characteristics of white silver metal, we found interesting results. Silver clay with 3% H_2O_2 exhibited the highest porosity and was the weakest in terms of mechanical strength. In contrast, silver clay with 30% H_2O_2 exhibited the lowest porosity and highest mechanical strength with low shrinkage on baking (Fig. 8). Mechanical strength of porous silver metal was almost same as that of solid silver metal, whereas volume contraction of porous one was lower than that of solid one (Fig. 5A and 8). The reason for this could be due to their porosity. In 30% H_2O_2-treated samples, large bubbles were diminished and small ones remained (Fig. 7). In contrast, large bubbles remained in the metal with 3% of H_2O_2 (Fig. 7). Though distilled water (DW) did not contain any foaming agents, silver clay with distilled water (0% of H_2O_2) exhibited 7–8% of porosity (Fig. 8). These bubble might appear in boiling of DW during baking silver clay and/or get into silver clay when mixture of silver powder and DW. Using this porous white metal, we could make metal-lined ceramic crowns within only 30 min, if ceramic crown caps were prepared as ready made goods. This suggests the possibility that esthetic prosthesis instead of temporary prosthesis should be made by chair side immediately after removal of orthodontic appliances. The results of experiments probing the mechanical strength of combinations of ceramics and white-colored silver metals showed that a lining of silver metal applied to an alumina ceramic plate made the breaking point and resilience higher (Fig. 9A and B). Lining porous metals on ceramics showed strengthened mechanical characteristics compared to the lining non-porous samples. The reason for this should be the adherence of porous metals to ceramic plates after breaking of ceramic plates even in the region of 5 mm from the alumina fracture point, in contrast to the situation found with non-porous metals, which became detached (Fig. 10). After white-colored silver metal heated at 700 °C on zirconia plate, solid metal could detached from ziriconia plate easily, however, strong force was needed to detach the porous one from the ceramic plate with remaining of porous one (Fig. 6). These results suggested that this metal-combined ceramics could be used for reinforcement and prevention of crushing of the ceramic orthodontic appliances.

Table 3 – Vertical slot sizes of non- and white color-treated orthodontic brackets.

	Non-treated bracket	White color-treated bracket
Center of slot size (mm)	0.534 ± 0.002	0.533 ± 0.001[a]

$n = 8$.

[a] Not statistically significant between non-treated and white colored bracket.

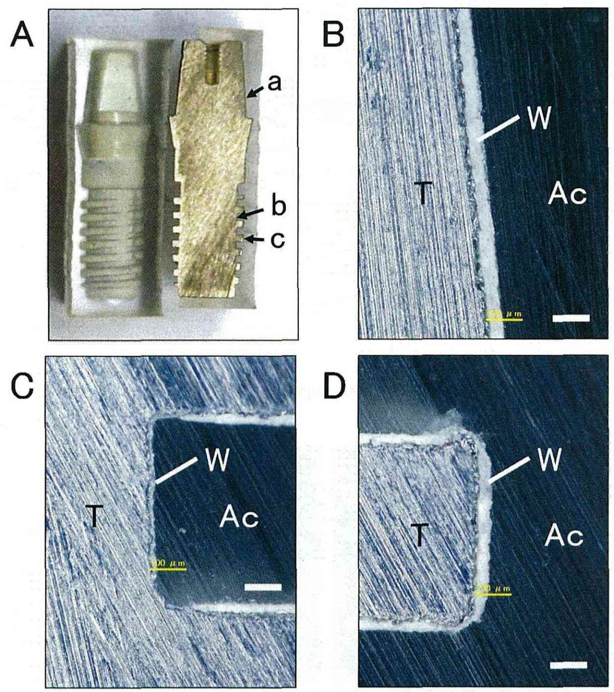

Fig. 11 – Cross sectional photos of white colored dental implant. (A) Observation part of cross sectional photo of dental implant. (a) Mirror polished abutment part, (b) sand blasting of the deepest part of the screw thread of fixture part, (c) sand blasting of the top part of the screw thread of fixture part. (B) High magnification (100×) of "a" part of "A". (C) High magnification (100×) of "b" part of "A". (D) High magnification (100×) of "c" part of "A". T, titanium of the dental implant; W, white color part of the dental implant; Ac, acrylic resin for embedding of the dental implant; in B–D. White bars in B–D indicated 100 μm.

For the use of white-colored metals for dental appliances including orthodontic appliances, we developed a white-colored surface preparation method for titanium metal. Fig. 4 represents the white color prepared dental products. Evaluation of thickness of white color layer of dental implant revealed that rank order of thickness was mirror polished abutment part > sand blasting of the top part of the screw thread of fixture part > sand blasting of the deepest part of the screw thread of fixture part. This results indicated that white color layer could be created on any condition of titanium metal, and their thickness was 10–50 μm which was enough for white appearance recognized by naked eyes (Fig. 11; Table 4). However, there were two problems with this method. One was the difficulty of setting appropriate conditions of white preparation, because if the conditions strayed from the appropriate conditions, the white-colored surface could be worn off by the external forces. However, if we could find appropriate conditions, the white-colored surface should not be worn off by vigorous scratching and strong external forces (data not shown). Another problem was that the white-colored surface became higher strength but fragile during its preparation (Fig. 5B). This could be due to the heat treatment. Titanium changes from the alpha phase (hexagonal close-packed structure) to beta phase (body-centered cubic lattice) at 885 °C [14]. In this change of structure, mechanical strength of titanium could be decreased. However, this method changed only the surface of titanium, so that the sizes of objects were not altered (Table 3). This should be one of the biggest advantage of this white-colored preparation method.

Table 4 – Thickness of three part of white part in the dental implant.

	Thickness (μm)
a	44.5 ± 5.6
b	13.9 ± 2.2
c	31.7 ± 3.7

"a", "b" and "c" correspond to the parts of 'a", "b" and "c" of the dental implant in Fig. 11A, respectively. a, mirror polishing part; b, sand blasting of the deepest part of the screw thread; c, sand blasting of the top part of the screw thread.
$n = 5$.

To clarify the causes of this white coloration of the metals, we performed component analysis using an electron probe microanalyzer. We had considered that the reason for this white color was due to the oxidation of the metals; however, surprisingly no oxide was found in white silver metal (Table 5). Carbon, phosphorus and calcium are the result of some contamination (Table 6). Their contamination into the white metal could be prevented using a single purpose furnace under more restricted condition. From this result, we could not say anything about the mechanisms of white coloration of silver metal except in terms of micro-diffused reflection. In titanium metals, the white color of the titanium surface was due to rutile titanium dioxide (Table 6; Fig. 14). Anatase titanium dioxide could be created by baking titanium at 400–600 °C, besides rutile titanium dioxide could be created by baking at more than 800 °C [16]. Between 600 and 800 °C, titanium oxide was in an anatase and rutile mixed phase [16]. It is reasonable that our white titanium dioxide was rutile titanium dioxide. Anodic oxidation of titanium make titanium dioxide on the surface of titanium for improvement of corrosion resistance,

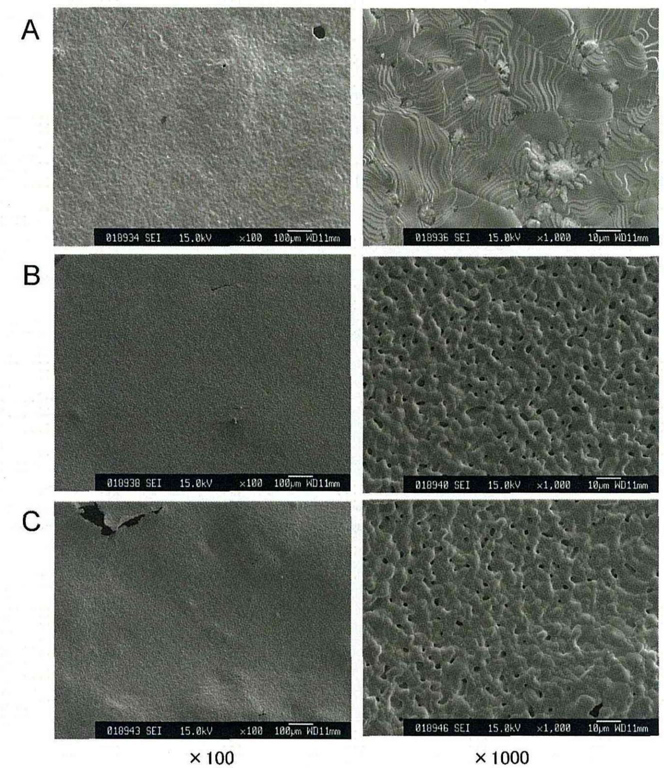

Fig. 12 – Scanning electron micrographs of silver and white-colored silver metal. (A) metal-colored silver, (B) white-colored solid silver metal, and (C) white-colored porous silver metal.

Table 5 – Components of white-colored silver metal.

Components	Solid silver (mass%)	Colored (at%)	Solidwhite (mass%)	Colored (at%)	Foamed white (mass%)	Colored (at%)
Ag	99.319	94.196	98.817	93.582	99.372	94.633
C	0.681	5.804	0.531	4.509	0.628	5.367
P	–	–	0.328	1.081	–	–
Ca	–	–	0.324	0.828	–	–
Total	100.000	100.000	100.000	100.000	100.000	100.000

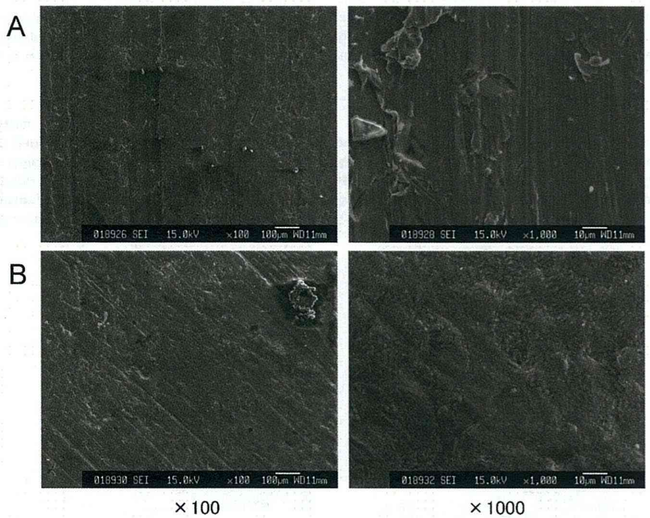

Fig. 13 – Scanning electron micrographs of non- and white color-treated titanium metal, (A) non-treated titanium metal, (B) white color-prepared titanium metal.

which contained anatase titanium dioxide [5–8,15]. Anodic oxidation of titanium also color the titanium surface [8]. These results and reports suggested that method in this paper, i.e. atmospheric oxidation, might be different way of oxidation from anodic oxidation, and change the metal top surface into metallic oxides which could be recognized white color appearances by naked eyes. In this process, the photorefractive effect should be involved, which is a nonlinear optical effect seen in the certain crystals and other materials that respond to light by altering their refractive index [17].

We have described the possibility of making white-colored metals for dental appliances in this paper. Further studies should be undertaken for practical applications; however they could be "win-win" solutions in reconciling the demands of both patients and doctors.

Table 6 – Components of white-color prepared titanium metal.

Components	Non (mass%)	Treated (at%)	White color (mass%)	Prepared (at%)
Ti	96.592	89.955	47.277	23.194
O	2.820	7.860	50.126	73.622
C	0.588	2.185	0.567	1.109
Na	–	–	2.030	2.075
Total	100.000	100.000	100.000	100.000

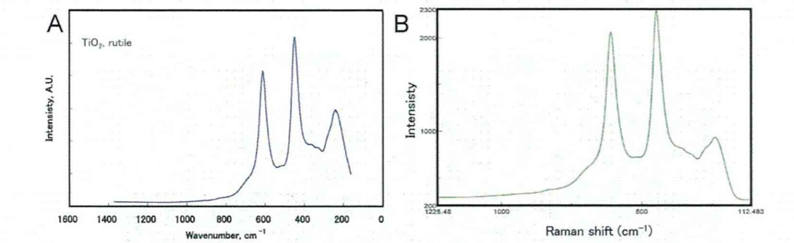

Fig. 14 – A laser Raman spectrum, (A) Raman spectrum of the rutile type of titanium dioxide. Data were obtained from RASMIN web (http://riodb.ibase.aist.go.jp/rasmin), (B) Raman spectrum of white color-prepared titanium. White-colored surface of titanium was rutile type titanium dioxide.

5. Conclusions

We examined the possibility of making of white-colored metal for dental appliances. The results obtained in this study are as follows:

- Molding of a silver clay can generate white-colored metals by baking.
- White-colored surface preparation for titanium involved oxidation of the surface of titanium, and the oxide possessed the rutile structure.

These methods should cope with both esthetics and mechanical strength including the strength of dental devices including orthodontic appliances.

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Ⅲ．研究成果の刊行に関する資料⑥

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A new method for fabricating zirconia copings using a Nd:YVO$_4$ nanosecond laser

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The purpose of this work was to fabricate zirconia copings from fully sintered Y-TZP blocks using a Nd:YVO$_4$ nanosecond laser in order to avoid complicated procedures using conventional CAD/CAM systems. To determine the most appropriate power level of a Nd:YVO$_4$ laser, cuboid fully sintered Y-TZP specimens were irradiated at six different average power levels. One-way ANOVAs for the average surface roughness and laser machining depth revealed that an average power level of 7.5 W generated a smooth machined surface with high machining efficiency. Y-TZP copings were then machined using the proposed method with the most appropriate power level. As the number of machining iterations increased, the convergence angles decreased significantly ($p<0.01$). The accuracy of the machined copings was judged to be good based on 3D measurements and traditional metal die methods. The proposed method using the nanosecond laser was demonstrated to be useful for fabricating copings from fully sintered Y-TZP.

Keywords: Y-TZP, CAD/CAM, Zirconia, Laser, Nd:YVO$_4$

INTRODUCTION

Recently, dentists and patients have become interested in all-ceramic restorations, which do not contain metals, which block light transmission, and better resemble the natural tooth appearance than any other restorative option[1]. In addition, all-ceramic restorations do not cause metal allergy problems. The clinical shortcomings of ceramic materials, such as brittleness, low tensile strength, and marginal inaccuracy, continue to limit their use compared to porcelain-fused-to-metal crowns[2,3]. Nevertheless, patients' demand for improved esthetics has driven the development of ceramic restorations. The use of all-ceramic restorations has spread as a result of the application of high-strength ceramics, such as zirconia, to the coping materials.

Zirconia ceramics for dental restorations have high strength and high toughness, which allows these materials to be used as all-ceramic coping materials for long-span bridges. However, machining fully sintered zirconia by milling is very difficult because of its high hardness. The coping is fabricated with an established method using a CAD/CAM system in which a partially sintered zirconia block is milled and subsequently sintered in a furnace. A linear shrinkage of 15 to 30% occurs due to sintering[4]. The increased milling efficiency of the softer partially sintered block has the trade-off of a potentially poorer fit caused by the sintering shrinkage, the scanning process, compensatory software design, and milling[5]. In order to avoid these complicated procedures, we have devised a new simple method by which to machine high-hardness zirconia using a laser. A range of lasers is now available in dentistry. The Nd:YAG laser can be used in the dental laboratory for laser welding. Metal parts such as frameworks can be joined by self-welding of the parts with combustible acrylic denture base resins and artificial composite teeth, which would be burned by conventional soldering[6]. Noda *et al.* conducted an experiment involving the irradiation of zirconia using this Nd:YAG laser and examined the possibility of welding zirconia[7]. They reported that laser irradiation induced cracking on the surfaces of zirconia so Nd:YAG dental laser welding should not be performed on zirconia[7]. Nd:YAG dental laser irradiation, which produced a millisecond-order pulse width, generated thermal effects on zirconia[8].

Therefore, we devised a new method by which to machine zirconia copings using an industrial Nd:YVO$_4$ Q-switched nanosecond laser, which had a smaller pulse width and a power density that was several hundred times higher than that of the conventional Nd:YAG dental laser. The purpose of the present study was to demonstrate the possibility of Nd:YVO$_4$ Q-switched nanosecond laser machining of zirconia copings.

MATERIALS AND METHODS

Nd:YVO$_4$ laser machine

In the present study, fully sintered yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) specimens were machined using a Q-switched Nd:YVO$_4$ (Neodymium Doped Yttrium Vanadate) laser machine (Lasertec 40, DMG, Berlin, Germany, Fig. 1) for fabricating the Y-TZP copings of all-ceramic restorations. This nanosecond laser machine generated a power density of 2.26×10^4 (kW/mm^2), which is several hundred times higher than a dental Nd:YAG laser with a millisecond pulse. The fundamental parameters of the Nd:YVO$_4$ laser machine are listed in Table 1.

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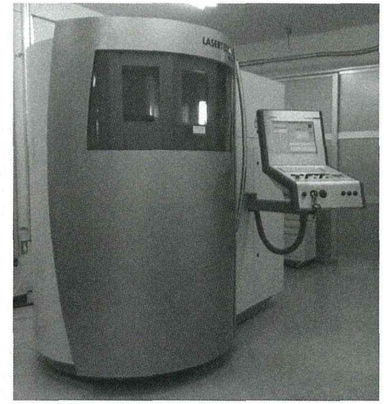

Fig. 1 Nd:YVO$_4$ laser machine.

Table 1 Specifications of the laser machine

Specification	Description
Laser type	Nd:YVO$_4$ crystal
Wave length	1,064 nm
Pulse width	18 ns
Operation mode	Q switched pulse
Scan speed	500 mm/s
Peak power	16 kW
Pulse frequency	50 kHz
Focus diameter	30 µm
Track distance	10 µm

Fully sintered yttria-stabilized tetragonal zirconia polycrystals (Y-TZP)

Two types of fully sintered Y-TZP specimens were prepared as follows. The discs of partially sintered Y-TZP (height: 25 mm, diameter: 98.5 mm, Aadva Zr disk, GC, Tokyo, Japan) were milled and subsequently sintered at 1,550°C for 18.5 h in a furnace using a dental CAD/CAM system (GM-1000, GC, Tokyo, Japan). Partially sintered Y-TZP consisted of >91 wt% ZrO$_2$, 5 wt% Y$_2$O$_3$, <3 wt% HfO$_2$, and <1 wt% Al$_2$O$_3$.

One cuboid (13 mm×13 mm×17 mm) fully sintered Y-TZP specimen was used to determine the most appropriate power level of the Nd:YVO$_4$ laser irradiation condition for fully sintered Y-TZP and another specimen (height: 7 mm, baseline: 10.6 mm), as shown in Fig. 2, was machined to form a Y-TZP coping on an abutment tooth of an imitation lower first molar.

Determination of the most appropriate power level of the Nd:YVO$_4$ laser

In order to determine the most appropriate power level of the Nd:YVO$_4$ laser, a cuboid fully sintered Y-TZP specimen was irradiated at six different average power levels (3, 6, 7.5, 9, 12, and 14 W). The irradiated surface area was square (2 mm×2 mm). The specimen was cleaned in distilled water using an ultrasonic cleaner. The machining depth and the calculated average roughness (Ra in µm) at each of the six power levels were evaluated. The machining depth was measured using a measuring microscope (STM6, OLYMPUS,

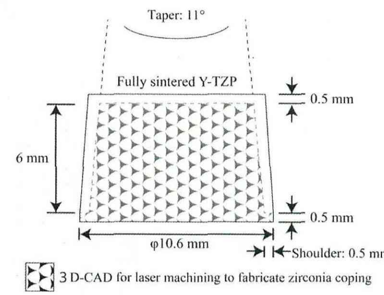

Fig. 2 Dimensions of the fully sintered Y-TZP specimen simulating a lower first molar, and 3D-CAD for laser machining to fabricate zirconia coping.

Tokyo, Japan). The calculated average roughness was also measured using a laser microscope (VK-8500, KEYENCE, Osaka, Japan) with a cut off value of 0.8 mm. One-way ANOVA and Tukey's multiple comparison test were used to analyze the data.

Machining Y-TZP copings using the Nd:YVO$_4$ laser machine

Machining 3D-CAD data of a Y-TZP coping were constructed using CAD software (Rhinoceros4.0, Robert McNeel & Associates, WA, USA). Y-TZP copings were machined in order to create the final form with a convergence angle of 11°, a cervical width of 10.6 mm, and a shoulder part width of 0.5 mm using 3D-CAD data (Fig. 2). The part that touched the abutment tooth, as shown in Fig. 2, was machined. Y-TZP copings were fabricated from fully sintered blocks using the Nd:YVO$_4$ laser machine with an optimal machining condition