Study on fabrication of orthodontic brackets with the photocatalytic function of titanium dioxide

Yosuke SATO¹, Ken MIYAZAWA¹, Natsu SATO¹, Kenjiro NAKANO², Yukiko TAKEI², Tatsushi KAWAI² and Shigemi GOTO¹

¹Department of Orthodontics, School of Dentistry, Aichi-Gakuin University, 2-11 Suemori-dori, Chikusa-ku, Nagoya 464-8651, Japan

²Department of Dental Material Science, School of Dentistry, Aichi-Gakuin University, 2-11 Suemori-dori, Chikusa-ku, Nagoya 464-8651, Japan

Corresponding author, Yosuke SATO; E-mail: yo_suke0910@yahoo.co.jp

We sought to investigate whether the photocatalytic function of rutile-type titanium dioxide is applicable for orthodontic brackets. To this end, TiO₂ specimens were compressed and sintered. Then, each specimen was analyzed by X-ray diffraction to confirm that no compositional changes had taken place. Next, the surface of each specimen was observed with a colorimeter, scanning electron microscope (SEM), and atomic force microscope (AFM). Fundamental material properties after calcination were measured. The photocatalytic function was evaluated using the decolorization method with toluidine blue. The following were observed with the increase of calcinations temperature: growth of crystal particles, decrease in surface roughness and surface brightness, but increase in shrinkage percentage and compressive strength. The aesthetic and mechanical properties of TiO₂ material were adequate when compared with other bracket materials. In addition, it had a satisfactory photocatalytic function after high-temperature calcination. Based on the favorable results obtained, rutile-type titanium dioxide seemed to be applicable for the fabrication of self-cleaning orthodontic brackets.

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INTRODUCTION

Plaque control is especially important during orthodontic treatment. The areas of teeth near the brackets or wires are difficult to keep clean. As a result, dental plaque or debris easily accumulates, which may then cause dental caries or periodontal diseases^{1,2}. In light of these problems, it would be highly desirable for a bracket material to possess a property that helps to prevent the adhesion of dental plaque or to disintegrate any adhesive products. This type of brackets will be greatly beneficial in the prevention of oral diseases during orthodontic treatment.

It is well known that titanium dioxide (TiO₂) has photocatalytic properties which decompose pollutants or prevent the harboring of pathogenic microorganisms³. Therefore, many kinds of products which contain titanium were developed to keep the products themselves clean or to decontaminate the environment. For example, air purifiers, non-discoloring paints, and teeth whitening are commercial products representative of the uses of TiO₂⁴⁻⁶.

Against this background, the authors decided to develop a new, TiO₂-containing bracket material which had a photocatalytic property. To examine whether the new bracket material demonstrated the intended properties for clinical use, disk-shaped specimens were sintered with a starting product that was composed of needle-like powder particles of TiO₂.

MATERIALS AND METHODS

Experimental material

Rutile-type titanium dioxide (FTL-100, Ishihara Sangyo Co. Ltd., Kanagawa, Japan) was used as the starting product for this experiment. Needle-shape structures of 0.2–0.3 μm diameter and 5–6 μm length were thus investigated.

Shape-forming of specimens

Specimens of two different shapes were prepared: disks and cylinders (Fig. 1). For the disk specimens, TiO₂ powder was added to a die 12 mm in diameter and pressurized at 40 MPa for 1 minute. Then, the compressed materials were shaped to a disk 12 mm in diameter and 3 mm in thickness (Fig. 1a). For mechanical testing, cylindrical specimens 4 mm in diameter and 8 mm in height were prepared (Fig. 1b). For the cylindrical specimens, TiO₂ powder was added to a die 4 mm in diameter and pressurized at 566 MPa for 1 minute.

Sintering

The compressed disk specimens were sintered under air atmosphere at 1300°C, 1400°C, or 1500°C and maintained for calcination. The process is shown in Fig. 2. Compressed TiO₂ specimens were sintered at 1300°C, 1400°C, or 1500°C and maintained for calcination. The specimens were passively cooled at room temperature before the experiment. After the specimens were cooled down to room temperature, they were kept in a desiccator before use.

Fig. 1 Two different shapes of specimens: (a) disk specimen of 12 mm diameter and 3 mm thickness; and (b) cylindrical specimen of 4 mm diameter and 8 mm height.

Compositions of TiO_2 sintered bodies

The X-ray diffraction (XRD) patterns of the titanium dioxide obtained from experiments at various temperatures were recorded from $5^\circ 2\theta$ to $110^\circ 2\theta$ with a diffractometer (Rigaku RAD-RC, Tokyo, Japan) operated at 40 kV and 60 mA, producing $\text{CuK}\alpha 1$ radiation at a scan speed of $2^\circ/\text{min}^{7,8}$. The relative intensities were determined as diffraction line heights relative to the three intense lines normalized to the most intense line with the diffraction data book.

Evaluation of color difference

The color values of all disk specimens were measured by means of a colorimeter (Chroma Meter CR-200, Minolta, Osaka, Japan). L^* , a^* , and b^* values were obtained according to the color space of CIE 1976 $L^*a^*b^*$ ^{9,10}.

Surface texture observation of titanium dioxide specimens

The surface of each titanium dioxide specimen was observed using a scanning electron microscope (SEM; JSM-5900LV, JEOL, Tokyo, Japan) at $\times 5,000$ magnification¹¹. Acceleration voltage of the SEM was 5 kV.

Surface roughness (R_a)

The R_a value of each specimen was defined as the arithmetic average value of all absolute distances of the roughness profile from the center line within the measuring length. All measurements were performed using an atomic force microscope (AFM; SPM-9500, Shimadzu, Tokyo, Japan)¹²⁻¹⁴. For each sintering temperature, five disk specimens were measured.

Sintering shrinkage

Shrinkage ratio was derived from measurements between the sintered specimen and the original one ($\phi 12 \text{ mm} \times 3 \text{ mm}$)¹⁵. These ratios were normalized against the original specimen of 12 mm diameter and 3

Fig. 2 Sintering program of specimens.

mm thickness. Each specimen was measured at three points.

Mechanical tests

The cylindrical specimens calcinated at 1300°C , 1400°C , and 1500°C were tested to failure at a crosshead speed of 1 mm/min by an Instron testing machine (Instron 4481, USA)^{16,17}. Each experiment was repeated nine times. Compressive strength, maximum strain, and elastic modulus were measured by compressive stress-strain curves.

Evaluation of photocatalytic ability

The photocatalytic performance of specimens was evaluated using the decolorization method with toluidine blue. Each specimen was immersed into a 15-ml bottle containing 2% toluidine blue solution¹⁸. A bottle of toluidine blue solution without any specimen served as the control. Each specimen was

photoirradiated with 365-nm ultraviolet radiation using a handy UV Lamp (LUV-16, As One Corporation, Osaka, Japan) for 48 hours. The strength of ultraviolet rays was $1820 \mu\text{W}/\text{cm}^2$ when irradiated at 50 cm sideways from the sample.

When the immersion period was completed, the color change of each bottle was measured at 500 nm using an absorption spectrometer (Ultrospec 3000 UV-Visible spectrophotometer, Amersham Pharmacia, Cambridge, England). Each of these measurements was repeated six times and then normalized against distilled water. In addition, measurements were also performed when each bottle was covered with an aluminum foil.

Fabrication of an experimental bracket

An experimental bracket was fabricated in this study from a trimmed TiO_2 block.

RESULTS

Composition of TiO_2 sintered bodies

Figure 3 shows the X-ray diffraction (XRD) patterns of the specimens. The normalized relative intensities of

Fig. 3 X-ray diffraction (XRD) patterns of sintered specimens.

Fig. 4 Surface color of sintered and non-sintered specimen.

every specimen matched those of rutile-type TiO_2 .

Evaluation of color difference

Figure 4 shows the surface colors of the sintered and non-sintered specimens. The surface color of non-sintered specimen remained white, while those of the sintered specimens turned dark brown. Figure 5 shows the color difference results of each sintered specimen. L^* , a^* , and b^* values were significantly different as the

Fig. 5 Color difference as measured by means of a colorimeter ($n=5$).

Fig. 6 Surfaces of non-sintered specimen (a), specimen sintered at 1300°C (b), at 1400°C (c), and at 1500°C (d).

Fig. 7 Surface roughness (R_a) of each specimen measured using an atomic force microscope ($n=5$).

Fig. 8 Shrinkage ratios of sintered specimens ($n=10$).

Table 1 Mechanical strength and elastic modulus of sintered specimens

	1300°C	1400°C	1500°C
Mechanical strength [MPa]	52.32 (3.75) ^{a,b}	91.43 (10.21) ^{a,c}	152.63 (7.60) ^{b,c}
Elastic modulus [GPa]	5.54 (0.12) ^{d,e}	9.06 (0.09) ^{e,f}	13.42 (0.36) ^{d,f}

All values are indicated as the mean (SD) ($n=6$).
In each horizontal row, the same superscript letter indicates a significant difference at $p<0.01$ using ANOVA followed by the Bonferroni test.

sintering temperature increased ($p<0.01$).

Surface observation

Figure 6 shows the scanning electron images of the specimens. The non-sintered specimen (Fig. 6(a)) demonstrated the needle-shaped structures of titanium dioxide, with a lot of space interspersed throughout these needle complexes. Needle growth and adjacent needle adhesion appeared in the sintered specimen at 1300°C (Fig. 6(b)). A greater degree of needle adhesion to each other was observed in the sintered specimen at 1400°C (Fig. 6(c)), and tyloses were also observed. In the sintered specimen at 1500°C (Fig. 6(d)), no space was observed as a result of titanium dioxide adhesion.

Surface roughness

The R_a value of the sintered specimen at 1300°C was 356.9 nm. That at 1400°C was 291.5 nm, whereas that at 1500°C was 180.7 nm (Fig. 7). In other words, the higher the calcination temperature, the lower the surface roughness became. Based on the results obtained, there were significant differences in surface roughness among 1300°C, 1400°C, and 1500°C ($p<0.01$).

Sintering shrinkage

Figure 8 shows the shrinkage value of each sintered specimen. As the calcination temperature increased, the degree of shrinkage also likewise increased.

Mechanical tests

Table 1 shows the mechanical strength and elastic modulus values of each sintered specimen. As the calcinations temperature increased, so did the compressive strength.

Evaluation of photocatalytic ability

The bottles shown in Fig. 9 depict the results of each specimen immersed in toluidine blue solution and the control. The higher the calcination temperature, the more concentrated the toluidine blue solution became. It could be seen that the experimental groups demonstrated significantly higher photocatalytic ability than the control ($p<0.01$) (Fig. 10). As for the differences between each calcinations temperature *versus* that under a dark condition, these results were not admitted in this study.

Fig. 9 Toluidine blue solutions after irradiation with ultraviolet rays.

Fig. 10 Photocatalytic performance of specimens evaluated using decolorization method with toluidine blue.

Fig. 11 Experimental bracket, with photocatalytic function, fabricated from a trimmed TiO_2 block.

Fabrication of an experimental bracket

As shown in Fig. 11, an orthodontic bracket was prepared in this study by machining. Fracture of sharp edges and surface destruction were not observed in this experimental bracket.

DISCUSSION

Selection of starting material

In mainstream orthodontic treatment, the treatment plan is to move teeth to their corrected positions *via* wires applied to the orthodontic brackets. However, the control of dental plaque remains a formidable challenge, especially when increased susceptibility to dental caries or periodontal diseases in orthodontic patients cannot be ignored. Against this background, the development of self-cleaning brackets logically becomes a very important focus for intraoral health. In the present study, we focused our attention on the photocatalytic function of titanium dioxide with a view to developing orthodontic brackets that have the capability to degrade organic chemicals.

Titanium dioxide can exist in three crystalline forms: anatase, rutile, and brookite. The anatase-type and rutile-type have been utilized in practical applications, but the brookite-type is generally a subject of academic study. Among these three types, the anatase-type has the highest photocatalytic activity^{19–21}. However, the excitation wavelength is located on the UV side. Therefore, in the present study, the rutile-type with visible light excitation was employed.

In the preliminary experiment, the required strength failed to be achieved when sintering was conducted at 1200°C. For this reason, it became necessary to sinter at higher temperatures — which then further justified the use of rutile-type TiO_2 in this study as it exhibits stability at high temperatures.

Evaluation of sintered bodies

The TiO_2 specimens showed a tendency to shrink during sintering as the calcination temperature increased, such that the shrinkage percentage was 17.2% at 1500°C. This is a general property of ceramic materials which also applies for the calcination of dental porcelain, and which means that a lot of skill is needed to correct shrinkage during bracket preparation.

In the present study, the calcination of titanium dioxide at a high temperature resulted in a decrease in L^* and an increase in a^* . The b^* component also showed a tendency to increase except for the region between 1400°C and 1500°C. In other words, surface brightness decreased in conjunction with a shift to the red direction along the red-green axis and a shift to the yellow direction along the yellow-blue axis. Due to these changes, the surfaces of the sintered specimens became dark brown, and it was also probable that the sintered specimens became nitrided. For aesthetic brackets, their color should ideally match those of natural teeth. On this note, the calcination temperature should take into account not only its effect on mechanical strength, but also on color change, when the calcination temperature is increased.

In the present study, pre-calcination compression molding was conducted to achieve higher compressive strength. In this manner, high-density pre-calcination specimens were prepared for sintering. Through observation by means of a SEM and an atomic force microscope (AFM), the following were observed: growth of crystal particles, increase in interparticle contact area, and reduced surface roughness. These results were aligned with the increase in compressive strength as the calcination temperature increased. Most notably, the compressive strength achieved by the sintered material in the present study was sufficient to withstand the machining during the fabrication of orthodontic brackets^{22–25}.

The elastic moduli of TiO_2 sintered bodies were 5.54 GPa at 1300°C and 13.42 GPa at 1500°C. Thus, there was an increasing trend in elastic modulus as the calcination temperature increased. In light of the 13.42 GPa elastic modulus achieved at 1500°C, it was thought that a clinical application seemed possible because the elastic modulus of the sintered body was similar to that of dentin.

In view of the evaluation findings of the sintered TiO_2 bodies, the sintered material in the present study satisfactorily met the requirements for the fabrication of orthodontic brackets.

Evaluation of photocatalytic activity of calcined specimens

The photocatalytic activity of titanium dioxide tended to decrease as the calcination temperature increased. However, no changes in the crystal structure were observed by X-ray diffraction. Thus, it was thought that the decrease in the photocatalytic activity of the sintered bodies was due to the following factors: growth

of crystal particles, decrease in the size of interparticle pores, and decrease in surface area — which was due to reduced surface roughness brought about by the increase in calcination temperature. However, the decolorization test with toluidine blue solution revealed that a sufficient photocatalytic effect was still present, even for the specimen sintered at 1500°C. Based on the photocatalysis results, it was thought that the sintered material in the present study could fulfill the self-cleaning requirement of orthodontic brackets.

In the present study, it has been shown that aesthetic and self-cleaning brackets could be developed. In terms of the adequacy of mechanical properties, the minimum requirements were fulfilled under the calcination conditions of the present experiment. Nonetheless, we also consider that it is possible to prepare stronger ceramics by a combination of materials.

The applicability of TiO₂ in orthodontic treatment

During ongoing orthodontic treatment, dental caries and white spot lesions are an unwelcoming development. To tackle this problem, Yamada *et al.*²⁶⁾ reported that the veneer might have a caries preventive effect by not only physically protecting the enamel, but also by strengthening the enamel with fluoride even when oral hygiene is markedly reduced during orthodontic treatment²⁷⁻²⁹⁾. By the same token, TiO₂ in orthodontic brackets can be doped with fluorine to achieve the antibacterial effect and hence prevent dental caries development.

On the form of orthodontic brackets, many reports abound. Amongst which, Rhodes *et al.*³⁰⁾ reported that if excessive tipping force were required by the clinician, ceramic brackets would be prone to fracture.

In conclusion, pertaining to the design of orthodontic brackets, the different considerations have been duly reviewed and examined in this study.

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