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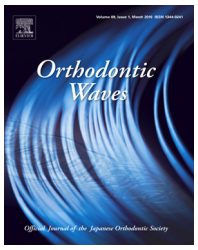

Research paper

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

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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.

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 $\varphi \times$ 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 $\Delta E^* ab$ (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:

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

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