Dental arch wires with tooth-like color

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(Received July 1, 2011, Revised February 26, 2012, Accepted February 27, 2012)

Abstract. Unique tooth-like (milky white) color *β-Ti* dental arch wires are prepared by anodization in a 1M H_2SO_4 electrolyte at 30°C and 30 V for 88 min and 40 s. Aggregates are formed on these surfaces of the anodized wires with tooth-like colors, and the results are different from those of the anodized wires with monochromatic colors which have smooth oxide surfaces. Similar to the monochromatic wires, the composition of the oxide layer is TiO_{2-x} and the x approaches zero at the outer layer. But different from the amorphous structure observed in monochromatic wires, the oxide layers are partially crystallized with an anatase structure. The milky white colors result from the rough and crystalized oxide layers, not by the interference effect as observed in monochromatic wires.

Keywords: orthodontic materials; surface properties; anodization; tooth color

1. Introduction

Beta titanium, nickel-titanium and stainless steel dental arch wires are often used for orthodontic treatments (Kusy and Stush 1987, Whitters *et al.* 1999, Kwon *et al.* 2005, Walker *et al.* 2007). Colorization of dental arch wires has been reported previously (Yang *et al.* 2006, Wu *et al.* 2009), with the different colors of anodized wires resulting from optical interference (Yang *et al.* 2006, Wu *et al.* 2009, Aladjem 1973, Gaul 1993, Hrapovic *et al.* 2001). Anodization is a process of forming oxide on the metallic anode (Aladjem 1973). It has been found for a long time that metals can be colorized with anodization (Yang *et al.* 2006, Wu *et al.* 2009, Aladjem 1973, Gaul 1993, Hrapovic *et al.* 2001). Primarily for cosmetic reasons, arch wires with tooth-like colors are needed. This study investigates tooth-like (milky white) colors dental arch wires prepared by anodization (Chen *et al.* 2009). Since the interference effect does not produce milky white colors, the surfaces of the anodized wires are analyzed and the colorization mechanisms are illustrated.

2. Experimental procedures

β-Ti dental arch wire (#101-011, Ortho-Organizers, Carlsbad, CA, USA) was first polished with 1 μm alumina slurry, and cleaned with 0.2 M *HCl* solution, acetone and de-ionized (DI) water. The wire was then anodized with direct current (DC) in a 1 M H_2SO_4 electrolyte, and with *P*t as the

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cathode (Yang *et al.* 2006, Wu *et al.* 2009). The anodization was carried out at a constant voltage and constant temperature with different lengths of anodization time. Optical microscope and SEM (scanning electron microscopy, Hitachi, S-2500, Japan) were used to examine the microstructure and surface morphology of the specimens. XPS (X-ray Photoelectron Spectroscopy, ESCA PHI 1600, USA) was used to determine the chemical states of the elements in the oxide layer. Thickness of the oxide layer was measured based on the bright-field images obtained by TEM (transmission electron microscopy, Philips, TECNAI 20). The crystal structure of the oxide layer was characterized by TEM and GIXRD (grazing incidence X-ray diffraction, MAC Science, MXP18, Japan).

3. Results and discussion

Fig. 1(a) is an optical micrograph the *β-Ti* wire prior to anodization, showing its silver-gray metallic shine. Fig. 1(b) shows the *β-Ti* wire anodized at 30°C in the 1 M sodium sulfate solution at 60 V for 10 min, with a purple color in consistent with results reported previously (Yang *et al.* 2006, Wu *et al.* 2009). Fig. 1(c) is an optical micrograph of the *β-Ti* wire with a tooth-like (milky white) color which had been anodized at 30°C and 30 V for 88 min and 40 s. Similar results are found and tooth-like colors can also be observed in the *β-Ti* wires anodized at 40°C and 30 V for 80 min and 20°C and 60 V for 220 min, respectively.

The purple color of the anodized wires as shown in Fig. 1(b) and other colors mentioned in the

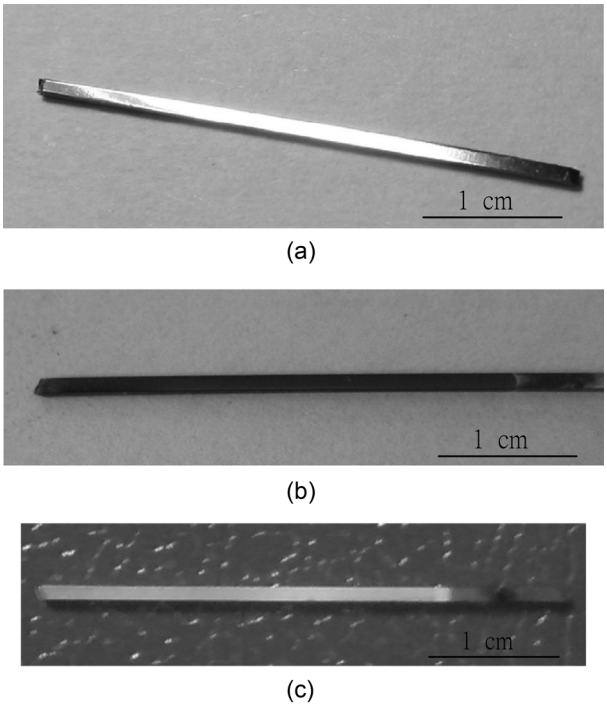

Fig. 1 Optical micrographs of *β-Ti* wire: (a) prior to anodization; (b) anodized in the 1M sodium sulfate solution at 30°C at 60 V for 10 min; (c) anodized at 30°C and 30 V for 88 min and 40 s

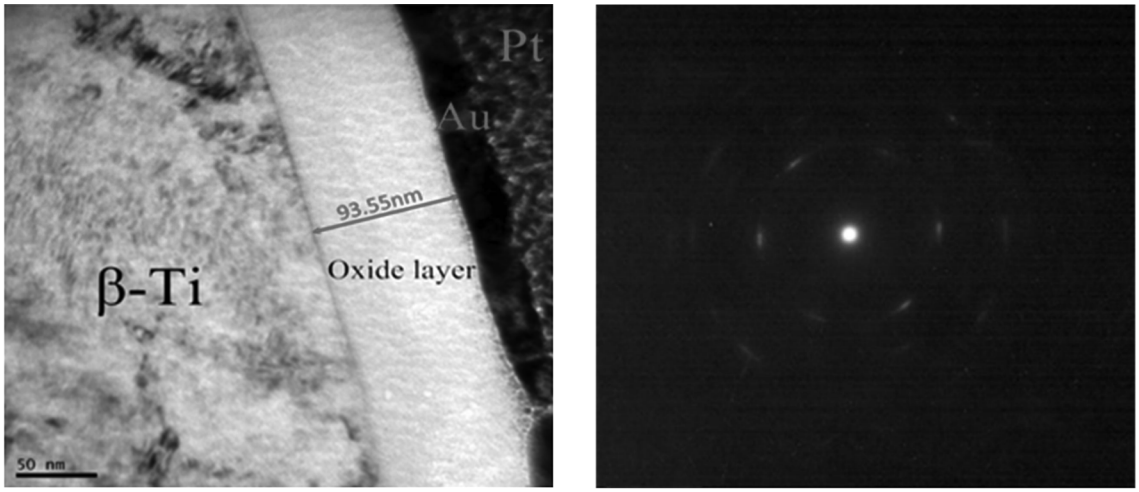

Fig. 2 Results of the *β-Ti* wire anodized at 30°C and 30 V for 88 min and 40 s: (a) TEM bright field image; (b) TEM selective area electron diffraction pattern of the oxide layer as shown in Fig. 2(a)

literature (Yang *et al.* 2006, Wu *et al.* 2009) are caused by the thin film interference effect. Through the constructive and destructive interference effects, the anodized wires thus display monochromatic colors (Yang *et al.* 2006, Wu *et al.* 2009). However, wires with a tooth-like (milky white) color, caused by a mixture of light with different wave lengths, cannot result from the interference effect. The *β-Ti* wire with a tooth-like color from anodization at 30°C and 30 V for 88 min and 40 s is then further analyzed to understand the colorization mechanisms.

Fig. 2(a) shows a TEM bright field image of the *β-Ti* wire anodized at 30°C and 30 V for 88 min and 40 s, and the thickness of the oxide layer is about 90 nm. Fig. 2(b) is the TEM selective area electron diffraction pattern of the oxide layer as shown in Fig. 2(a). A mixture of amorphous ring and diffraction spots are observed, indicating that the oxide layer has both crystalline and amorphous regions.

Fig. 3(a) shows the *Ti-2p* signal, i.e., the photoelectron signal of *Ti-2p* spin orbit, from XPS multiplex scan with argon ion bombardment. In the beginning of the bombardment, the peaks are from the titanium at the outer oxide layer and are at 459 eV and 465 eV which correspond to Ti^{+4} (Moulder *et al.* 1992, Carley *et al.* 1987). Thus, the composition of the outer oxide layer is TiO_2. As the bombardment time increases, the chemical states of *Ti* and *O* varies from outer to inner layers, and a general chemical formula of the oxide layer can be given as TiO_{2-x}, which are similar to those in the monochromatic color wires (Yang *et al.* 2006, Wu *et al.* 2009) Fig. 3(b) is its GIXRD graph. In addition to the 2θ peaks of *β-Ti* which are at 38.5°, 55.5° and 69.6°, the peaks of anatase TiO_2 phase at 25.4° and 48.0° are observed (JCPDS (Joint Committee on Powder Diffraction Standards) database, 44-1288(*β*-Ti) and 04-0477(anatase TiO_2)). These peaks from crystalline TiO_2 are not observed in the wires with monochromatic colors (Yang *et al.* 2006, Wu *et al.* 2009). These results indicate some parts of the oxide layer have been crystallized and the anatase TiO_2 phase is formed.

Fig. 3(c) is its secondary electron image (SEI) micrograph. Compared with the smooth oxide surfaces in the anodized wires with monochromatic colors (Yang *et al.* 2006, Wu *et al.* 2009), the

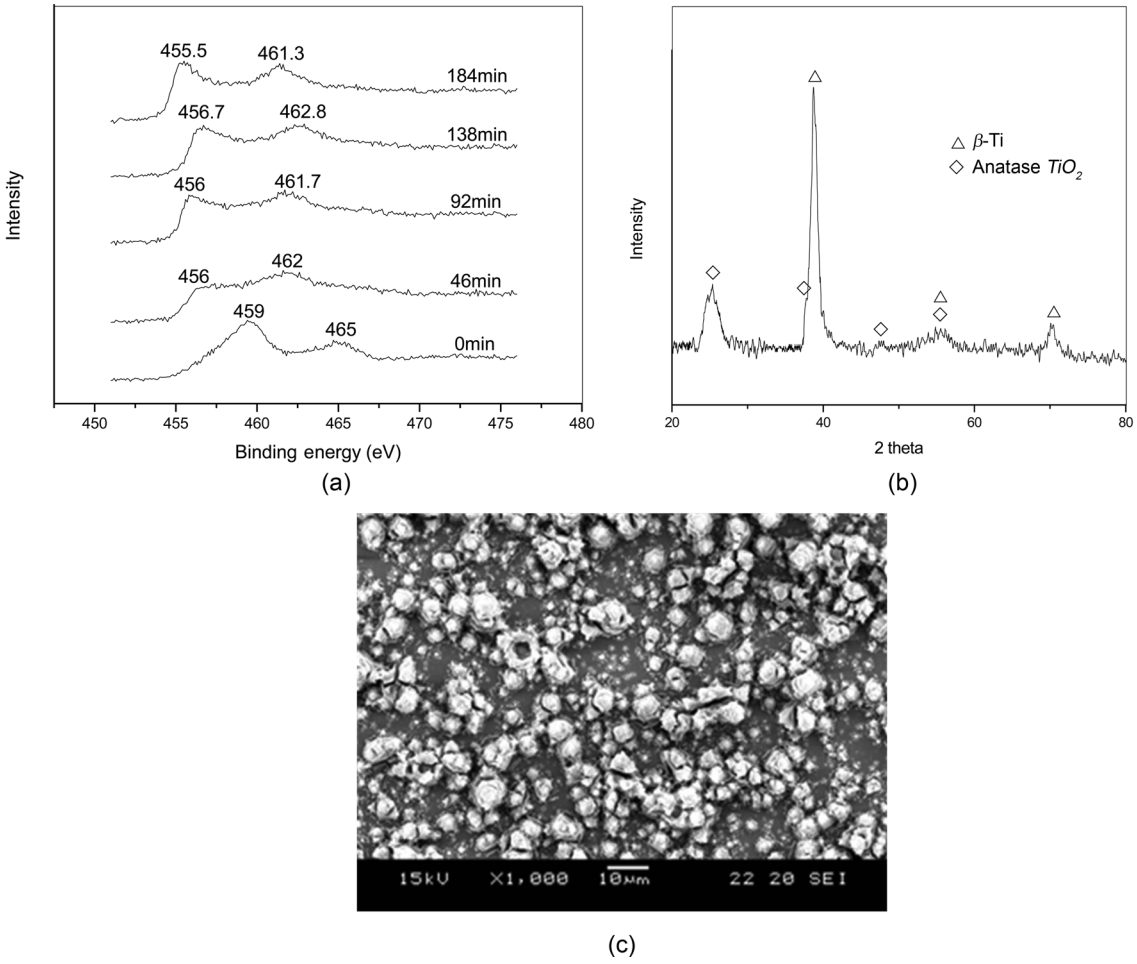

Fig. 3 Results of the *β-Ti* wire anodized at 30°C and 30 V for 88 min and 40 s: (a) *Ti-2p* signal from multiplex scan with argon ion bombardment; (b) GIXRD graph; and (c) SEI micrograph

surfaces of the wires with tooth-like colors are much rougher and have aggregates. A similar aggregate formation can also be observed on *β-Ti* wires anodized at 40°C and 30 V for 80 min and 20°C and 60 V for 220 min, and in the crystallization study of amorphous titanium oxide film (Nakamura *et al.* 2005). Although titanium oxides have different forms, such as rutile and anatase, the preferential formation of anatase in the amorphous titanium oxide film has been observed, and it is primarily due to the differences in their densities, which are 4.25, 3.89, and 3.8 g/cm^3, respectively (Nakamura *et al.* 2005).

Through anodization of the arch wires at various conditions, titanium oxide layers with certain thickness are produced on the surfaces. The anodized wires display various monochromatic colors which result from the interference effect (Yang *et al.* 2006, Wu *et al.* 2009). However, with longer anodization time, such as anodization at 30°C and 30 V for 88 min and 40 s, the outer part of the oxide layers are crystallized. Various aggregates are formed on the surface, and the surfaces are no longer smooth. Moreover, the refractive indices of TiO_2 in the amorphous and anatase phases are different (Bass *et al.*

2010). The multi-phase and rough surfaces weaken the interference effect and enhance light scattering, and tooth-like (milky white) colors are thus formed.

4. Conclusions

The *β-Ti* wires display monochromatic colors by anodization, and the colorization is caused by interference effect of the smooth and amorphous oxide layer. The amorphous oxide layer begins to crystallize with longer anodization time, and aggregates are formed on the surface. Because of the extensive light scattering, the interference effect is no longer the dominating optical factor, and the monochromatic colors of the anodized wires change to the tooth-like (milky white) colors.

Acknowledgments

This work was supported by the National Science Council of Taiwan (NSC96- 2218- E-007-012).

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