

Electropolishing of CP Titanium and Its Alloys in an Alcoholic Solution-based Electrolyte

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A newly developed electropolishing system, equipped with an original agitation function for an electrolyte and using a safe electrolyte composed of an alcoholic solution, was applied for wrought and cast CP titanium and its alloys. Surface roughness and morphology of the polished surfaces were then examined. Under an electrolytic condition of 70–75 V, 2.0 kA/m², and 30°C, wrought CP Ti and Ti-6Al-4V alloy achieved an apparent mirror-like finishing with an average surface roughness (Ra) of 0.03 and 0.12 μm respectively. Under the same condition, on the other hand, cast CP Ti and Ti-6Al-7Nb alloy produced rougher polished surfaces with average Ra values of 0.67–0.80 μm, and the finishing was apparently shiny, but not mirror-like. SEM observation of the polished surfaces showed that wrought CP Ti was even and completely featureless, while wrought Ti-6Al-4V alloy was pitted. For cast CP Ti, a needle-like phase containing traces of iron was observed on the polished surface.

Keywords: Titanium, Electropolishing, Surface roughness

INTRODUCTION

Titanium and its alloys have been widely used as materials for dental and biomedical applications, owing to their excellent mechanical properties and biocompatibility. For some of these applications, it is a mandatory requirement to smoothen and brighten the surfaces by polishing^{1–3}. To date, several polishing techniques have been applied⁴, namely mechanical polishing, chemical polishing, and electropolishing. However, for titanium and its alloys, a satisfactory finishing is hardly achieved due to some unique characteristics of titanium, such as existence of reaction layer, high chemical activity, and low thermal conductivity⁴.

Conventionally, mechanical polishing — occasionally incorporated with chemical polishing — is used for titanium castings^{5,6}. It should be mentioned that mechanical polishing with abrasives and buff is a complicated and tedious process for titanium, as compared with other dental alloys^{7,8}. Moreover, mechanical polishing may cause contamination of polished titanium surfaces^{9,10}. By contrast, electropolishing can microscopically provide a bright, clean, and smooth appearance when applied with an appropriately selected electrolyte and under the appropriate electrolytic conditions^{11,12}. This technique industrially applied to titanium has made use of electrolytes based on perchloric acid and hydrofluoric acid, which can cause hazardous effects¹². In dental practice, therefore, this technique has neither been applicable nor effective for titanium and its alloys.

Alcoholic solutions, an alternative option for electrolytes, are safe for application. This is because they reject the traditional usage of hazardous electrolytes. On this score, their industrial applicability for the electropolishing of titanium and its alloy have been explored recently^{13–16}. In the electropolishing of titanium with an alcoholic solution-based electrolyte, it has been reported that electrolyte agitation is an additional important factor to the removal of viscous layers that are easily formed on polished titanium surfaces^{15–8}. Indeed, in dental applications with alcoholic solutions, problems are reportedly encountered in the bid to achieve a uniform mirror-like finish for complicated dental titanium castings by the electropolishing technique^{19,20}.

Against this backdrop of problems and breakthroughs in the electropolishing of titanium, a novel apparatus for electropolishing was recently developed¹⁷. It was equipped with an original agitation function for the electrolyte, and whereby a safer electrolyte — composed of an alcoholic solution — was used for wrought and cast titanium and its alloys. In this study, the applicability of this newly developed electropolishing method was evaluated for titanium and its alloys from the viewpoints of surface roughness and morphology of polished surfaces.

MATERIALS AND METHODS

Wrought and cast specimens of titanium and its alloys

Table 1 shows the three kinds of commercially pure

(CP) Ti and two kinds of Ti alloys used in this study. CP Ti, JIS Class 2 (Code: T2W) and Ti-6Al-4V alloy, JIS Class 60 (Code: TVW) were wrought sheets with 2 mm thickness. T2W and TVW were cut into plate specimens of 20×50 mm dimensions. Surfaces of these plates were as-received. CP Ti of JIS Class 2 (Code: T2C), CP Ti of JIS Class 3 (Code: T3C), and Ti-6Al-7Nb alloy (Code: TNC) were for dental castings. T2C, T3C, and TNC were cast into plates ($20 \times 35 \times 1$ mm) with a magnesia-based investment (Titavest CB, J. Morita, Tokyo, Japan) at a mold temperature of 700°C using an argon arc casting machine (Cyclarc, J. Morita, Tokyo, Japan), according to manufacturer's instructions. Molds after casting were bench-cooled to room temperature and then divested. Cast specimens were sandblasted using $45\text{--}90\ \mu\text{m}$ glass beads at a pressure of 0.35 MPa for 30 seconds. All specimens prior to polishing were ultrasonically cleaned in isopropyl alcohol and subsequently in water. Both sides of the polished plates were partly covered with a masking tape to expose a total polished area of $10\ \text{cm}^2$.

Electropolishing apparatus and electrolyte

A non-aqueous electrolyte^{14,17,19} comprising ethyl alcohol (700 ml/L), isopropyl alcohol (300 ml/L), aluminum chloride (60 g/L), and zinc chloride (250 g/L) was prepared. A newly developed electropolishing apparatus¹⁷ (Prototype, Sanwa Industry Co. Ltd., Yamaguchi, Japan), as shown in Fig. 1, was employed. It was equipped with an agitation function and temperature control unit for the electrolyte. Size of tank was $250 \times 250 \times 250$ mm, but which could be modified to adapt to and accommodate large-sized workpieces in industrial use. A volume of 14 liters of the electrolyte was used for the tank. The original agitation function was performed by passing the electrolyte through a spouting plate connected to two metering pumps (flow rate at 25 L/min). A pair of curved meshes made of titanium was used as the cathode so that electrolyte flow would not be disturbed by agitation, as shown in Fig. 1(b). The curved shape was a semicircle of 50 mm diameter, 80 mm length, and 200 mm height, and the mesh shape was a diamond of 13 mm height and 7 mm width. The shortest distance between the two cathodes was 70 mm, and the distance between the cathode and

Table 1 CP Ti and Ti alloys used in this study

Code	Product name	Nominal composition	Manufacturer
T2W*	ST-50	CP Ti, JIS Class 2	Sumitomo Metal, Tokyo, Japan
TVW*	KS6-4	Ti-6Al-4V, JIS Class 60	Kobe Steel, Kobe, Japan
T2C**	Pure Titanium A	CP Ti, JIS Class 2	J. Morita, Tokyo, Japan
T3C**	Pure Titanium J3	CP Ti, JIS Class 3	J. Morita, Tokyo, Japan
TNC**	T-alloy Tough	Ti-6Al-7Nb	GC, Tokyo, Japan

*:wrought **:cast CP: commercially pure

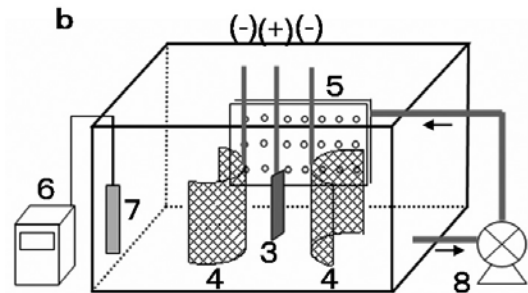
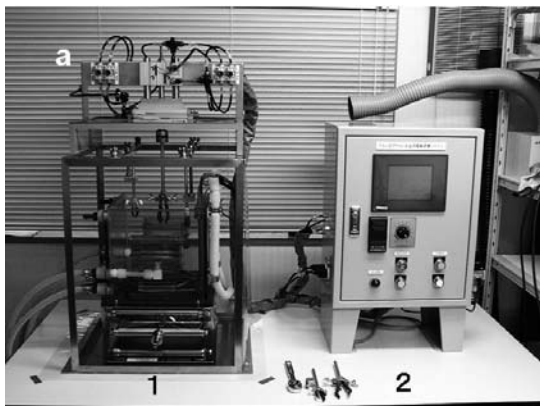


Fig. 1 Electropolishing apparatus used in this study. (a) Photograph of the apparatus; (b) Schematic drawing of electrolytic polishing operation, where 1: polishing apparatus; 2: controller unit; 3: anode (workpiece); 4: cathode; 5: spouting plate; 6: temperature control device; 7: cooling/heating coil; and 8: metering pump.

anode specimen was approximately 35 mm.

To examine the electropolishing parameters that would produce an apparent mirror-like surface for T2W and TVW, a direct current density of 0.9–3.7 kA/m² was applied with the electrolyte temperature held at 25, 30, and 35°C for 15 minutes. The electrolytic voltage was regulated to be constant. The apparent features of polished surfaces were macroscopically observed by the naked eye. Next, to evaluate the surface roughness and morphology of the polished surfaces for the five kinds of CP Ti and alloys used, electropolishing was performed under an electrolytic condition of 70–75 V, 2.0 kA/m², and 30°C for 15 minutes.

Surface roughness and morphology evaluation

After polishing, the specimens were washed with alcohol and then air-dried. Surface morphology was microscopically observed and analyzed by a field emission SEM (JSM-7000F, JEOL, Tokyo, Japan) equipped with an EDX analyzer. Surface roughness measurements were made using a profilometer (Surftest SJ-301, Mitutoyo, Kanagawa, Japan) according to JIS B0601:1994. Measurements were repeated three times for each group of specimens, and then the arithmetical mean roughness (Ra) obtained thereby. Data were statistically analyzed by one-way ANOVA followed by Scheffé's test.

RESULTS

Figure 2 shows the effects of electrolytic current-voltage and bath temperature on the apparent features of polished surfaces for T2W and TVW. Figure 3 shows the typical appearances of the different polished surfaces of T2W. When a direct current density of 1.2–2.4 kA/m² or 1.5–2.2 kA/m² was applied to T2W and TVW respectively with the electrolyte temperature held at 25 and 30°C, an apparently mirror-like surface was achieved for both sides of T2W and TVW plates, as shown in Fig. 3(a). When the electrolytic condition deviated from this electrolytic condition described above, a poor quality of a dull pickled surface with partly discolored or whitened areas was produced for both sides of the plate, as shown in Fig. 3(b).

Figure 4 shows the average surface roughness (Ra) values and their standard deviations before and after polishing. Figure 5 shows the degree of image clarity of polished surfaces for T2W and T2C. Statistically significant differences were found for the surface roughness values after polishing between the wrought group (T2W and TVW) and cast group (T2C, T3C, and TNC) ($p < 0.05$), while no statistically significant differences were observed among the cast specimen groups ($p > 0.05$). As for the wrought group specimens, T2W had the lowest Ra value of 0.03 μm

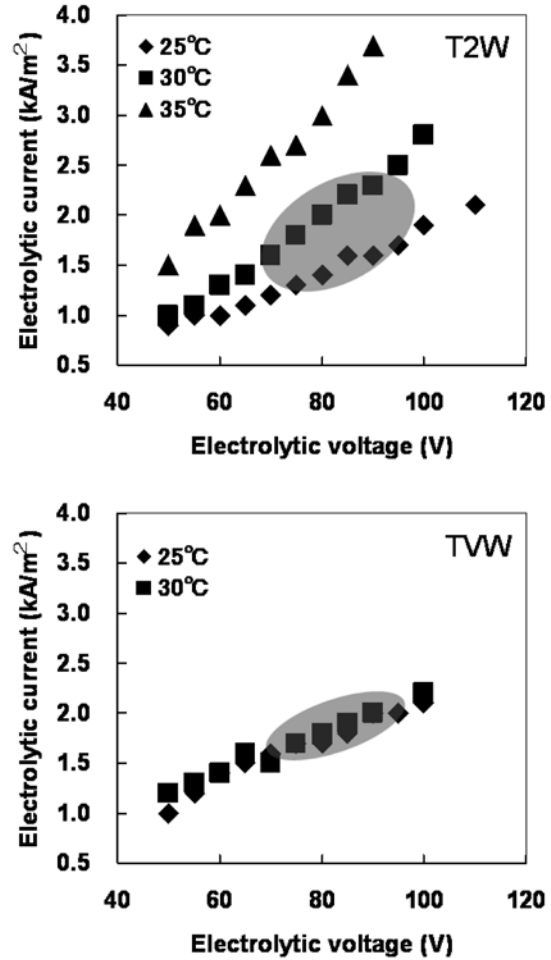


Fig. 2 Effects of electrolytic current-voltage and bath temperature on the apparent features of polished surfaces for T2W and TVW. Shaded areas show the electrolytic condition regions for producing an apparently mirror-like surface.

after polishing, and TVW also had a low Ra value of 0.12 μm after polishing. Further, as shown in Fig. 5(a), the polished surfaces of both T2W and TVW had an apparently mirror-like surface and clear image clarity. T2C, T3C, and TNC, on the other hand, produced rougher polished surfaces with average Ra values of 0.67 to 0.80 μm . Their surfaces were apparently shiny, but not mirror-like as that of T2W, hence exhibiting a poorer image clarity than T2W (Fig. 5(b)).

Figure 6 shows the typical SEM micrographs of the surfaces before and after the polishing of CP Ti and its alloys used. It could be observed from the SEM micrographs that T2W and TVW before polishing showed different features. Before polishing, T2W showed an uneven and concave surface with no streaks under high magnification (Fig. 6(a)), while

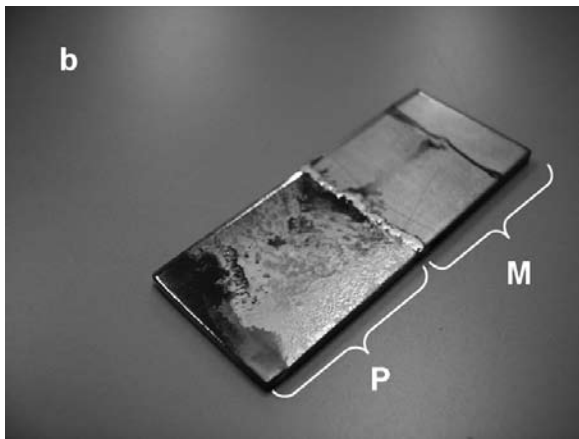
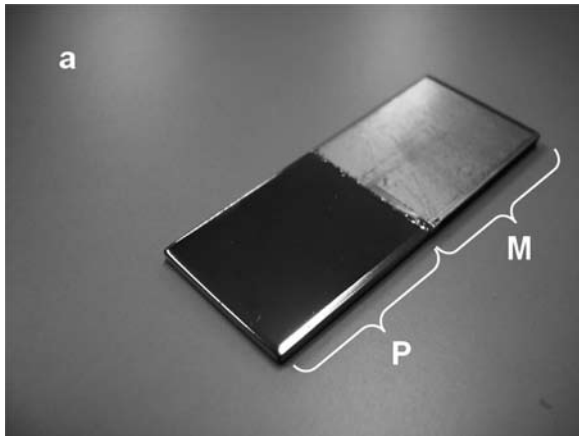


Fig. 3 Typical appearances of polished surfaces of T2W. (a) High quality of a mirror-like surface; (b) Poor quality of pickled surface. P: polished area; M: masked area.

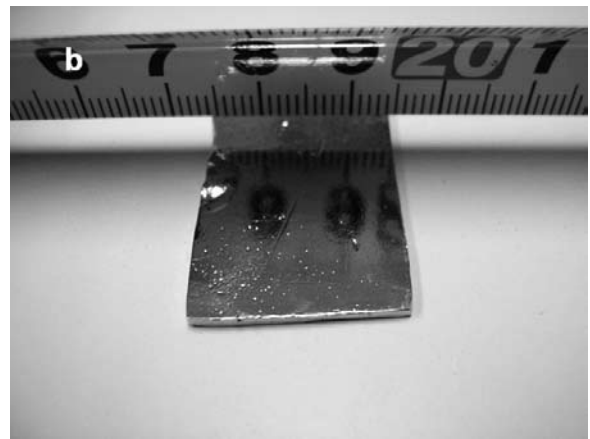
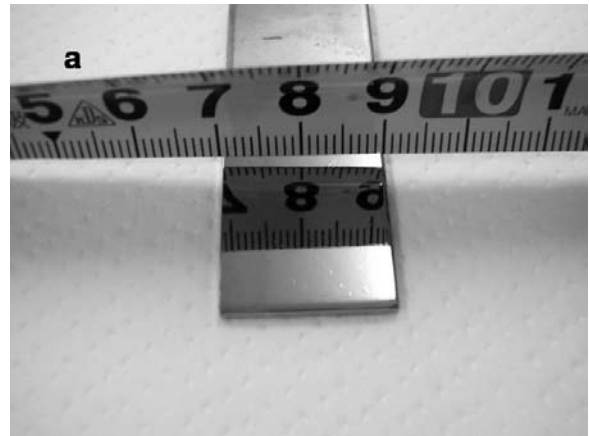


Fig. 5 Image clarity of the polished surfaces of: (a) T2W and (b) T2C.

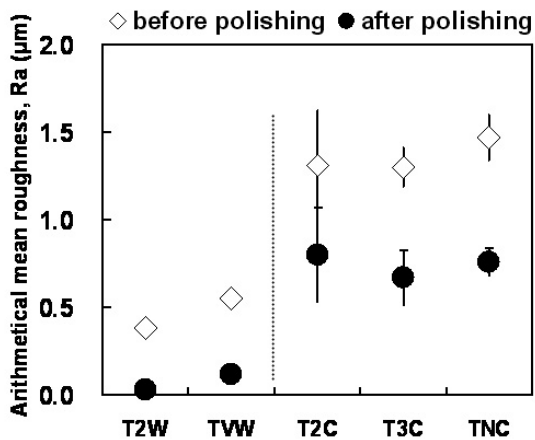


Fig. 4 Surface roughness (Ra) values before and after polishing.

TVW showed fine unevenness with streaks (Fig. 6(c)). The polished surface of T2W was even and completely featureless under high magnification (Fig. 6(b)), while the polished surface of TVW had many pits on the even surface (Fig. 6(d)). The sandblasted surface of T2C before polishing showed an uneven and rough surface (Fig. 6(e)), which was similar with those of T3C and TNC. Polishing of T2C and T3C yielded even surfaces with small amounts of fine dispersed needle-like phase (Figs. 6(f) and 6(g)), but polishing of TNC yielded an even and featureless surface without any second phase under high magnification (Fig. 6(h)). Figure 7 shows the EDX spectra of the polished surface of T2C. In the needle-like phase on the polished surface, traces of iron were detected, unlike the titanium matrix. T3C also showed a similar result as T2C.

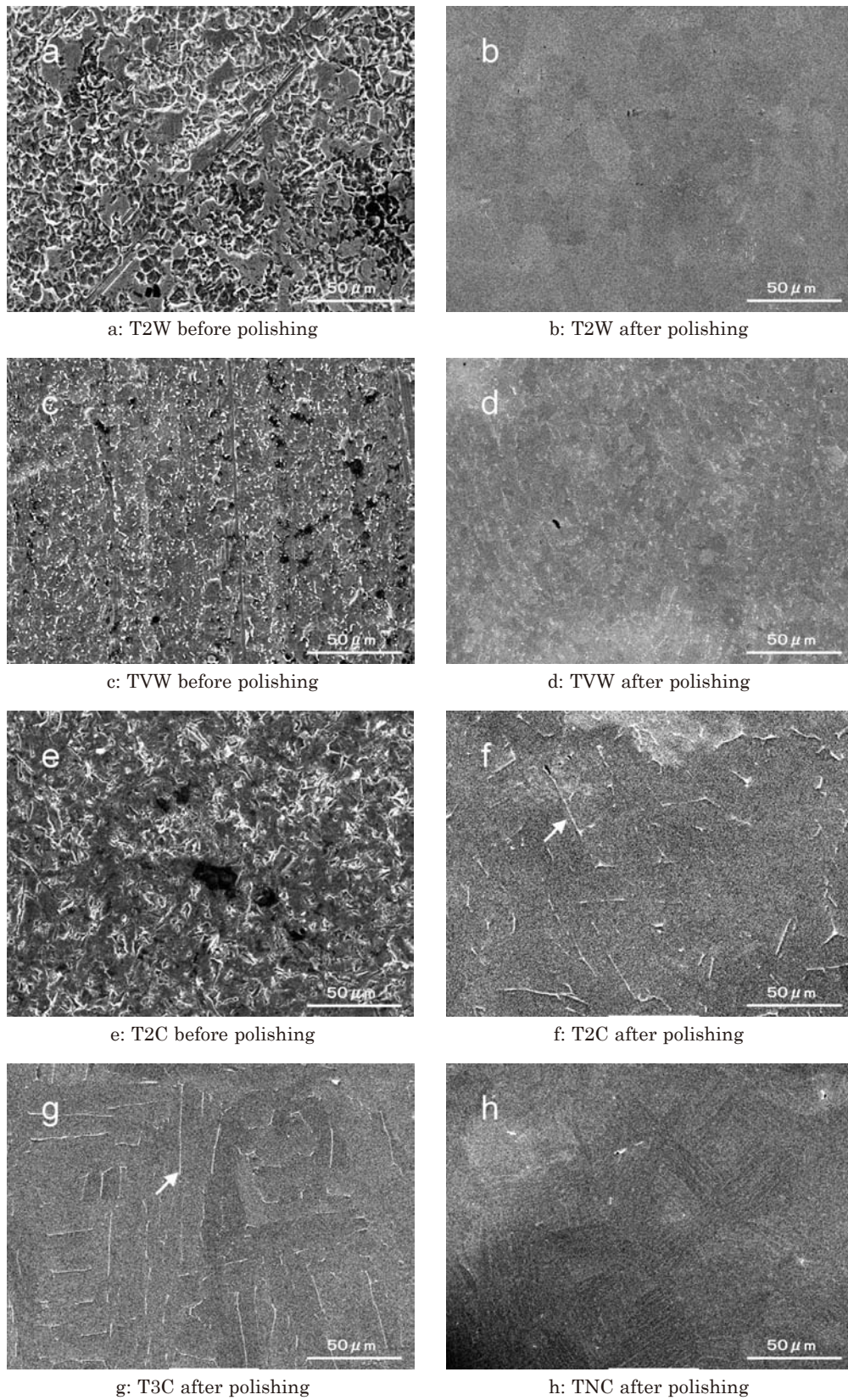


Fig. 6 SEM micrographs of the surfaces of CP Ti and its alloys before and after polishing. Arrows in (f) and (g) show a needle-like phase. (a) T2W before polishing; (b) T2W after polishing; (c) TVW before polishing; (d) TVW after polishing; (e) T2C before polishing; (f) T2C after polishing (g) T3C after polishing; and (h) TNC after polishing.

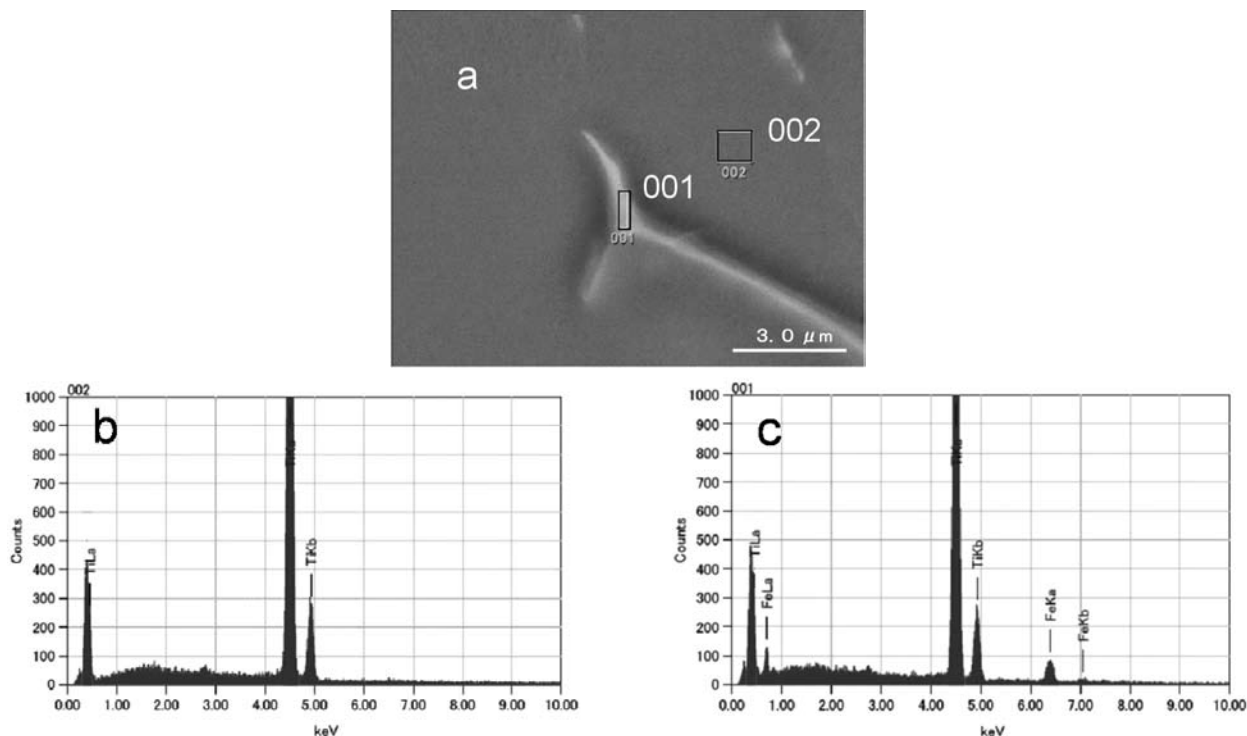


Fig. 7 SEM image and EDX spectra of the polished surface of T2C. (a) BEI; (b) spectrum from matrix (002 in (a)); (c) spectrum from second phase (001 in (a)).

DISCUSSION

Three basic reactions take place at the anode during the electropolishing of titanium¹²⁾:

Anode dissolution: $\text{Ti} = \text{Ti}^{4+} + 4\text{e}$

Oxygen evolution: $4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}$

Formation of a passive oxide film:



In the alcoholic solution used, titanium oxide and a viscous-colored layer, perhaps titanium chloride¹⁵⁾, were easily formed on the anode during the process¹⁵⁻¹⁷⁾. The viscous layer caused an impedance to the electropolishing process and resulted in a poorly finishing surface. Generally, electrolyte agitation is required to remove the bubbles and viscous layer from the surface and to refresh the electrolyte²¹⁾. Electrolyte agitation methods such as stirring with a magnet bar, vibration, and ultrasound have been generally used for smaller tanks. To produce good-quality, polished surfaces for titanium, the original method for large tanks might be required.

It should be highlighted that optimum polishing conditions for metals — which entail proper choices of electrolyte, current density, bath temperature, and polishing time — are not universally relevant^{11,12)}. In this study, under the electrolytic condition of 70–75

V, 2.0 kA/m², and 30°C, wrought CP Ti and Ti-6Al-4V alloy achieved apparently mirror-like surfaces, producing an average surface roughness of 0.03 and 0.12 μm respectively. In terms of average surface roughness, several preferred surface roughness threshold values have been suggested^{6,22,23)}. One such suggested surface roughness threshold value was 0.3–0.5 μm , which is also that of enamel surface in the oral cavity⁶⁾. Another suggested surface roughness values range was 0.09–0.2 μm , to the end of reducing bacterial adhesion and plaque colonization on titanium implants^{22,23)}. From the standpoint of proposed surface roughness threshold values, the electropolishing system seemed to be clinically acceptable for wrought titanium and its alloy based on the Ra values obtained. SEM observation, however, revealed pitting on the polished surface of wrought Ti-6Al-4V alloy. The surfaces of wrought T2W and TVW before electropolishing exhibited, microscopically, pickled and rolled features respectively. For wrought Ti and its alloy, the different manufacturing processes such as pickled or roll finishing might have influenced the microscopic features after electropolishing.

Cast titanium and its alloy were polished to a bright finish, but not to the same mirror finish as achieved for wrought titanium and its alloy. Further, increased surface roughness values of 0.67 to 0.80 μm were obtained. From the standpoint of proposed

surface roughness threshold values as described above, these surface roughness values appeared to be clinically unacceptable for the final finishing. Therefore, it seemed that electropolishing for cast titanium and its alloy, which were divested and sandblasted, was insufficient as a final finishing process.

Generally, deep scratches, undulation, rough unevenness, and mold-surface texture cannot be removed with electropolishing²⁴. The surface roughness of polished titanium castings, therefore, seem to be caused mainly by the inherently roughened casting surface which results from the investment material and casting conditions. For an effective finishing process to the end of obtaining a less rough electropolished surface, pretreatment to a rough surface before electropolishing appeared to be necessary with mechanical polishing. Alternatively, electropolishing would be an intermediate finishing process like chemical polishing^{5-7,25}, but not as a final finishing process in the dental practice.

T2C, T3C, and TNC showed similar macroscopic features and surface roughness values. However, SEM observation of polished T2C and T3C revealed finely dispersed needle-like phase containing traces of iron. Typically, iron is present in CP Ti as an inevitable impurity at a maximum content of 0.2 to 0.5%. Consequently, this residual iron can cause the formation of microscopic particles of beta phase in alpha matrix phase²⁶. Further, iron is a beta-stabilizing element for titanium²⁷. Therefore, the needle-like phase could be a beta phase. This phase could be formed in the cast specimens under a non-equilibrium cooling condition, and which could be attacked because of inherent differences in electrical potential between two phases. As a result, this non-uniform cast microstructure present in T2C and T3C accounted for the increased surface roughness of polished titanium castings, other than the inherent surface roughness of the castings prior to polishing as described above.

In conclusion, the newly developed electropolishing apparatus with an alcoholic solution-based electrolyte could produce an acceptable finishing for wrought CP Ti and its alloy, but not for cast CP Ti and its alloy. To the end of achieving effective final polishing for cast CP Ti and its alloy, it was necessary to further examine the effect of pretreatment on their inherent surface roughness prior to electropolishing. Separately, the variables of polishing processes also influence the rate of metal removal, other than surface roughness^{11,12}. On this score, further research is still needed to examine the effect on metal removal by electropolishing.

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