Original paper

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Surface Composition and Structure of Titanium Polished with Aqueous Slurry of Ferric Oxide

Rowshan AKHTER, Seigo OKAWA[1], Syuji NAKANO[1],
Masayoshi KOBAYASHI[2] and Osamu MIYAKAWA[1]
Chemistry of Dental Materials, Dhaka Dental College and Hospital,
Ramna-1000, Dahka, Bangladesh
[1]Department of Dental Materials and Technology,
Faculty of Dentistry, Niigata University
[2]EMX Laboratory, Niigata University
Gakkou-cho 2-5274, Niigata 951-8514, Japan

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Cast plates were prepared from commercial titanium. The plates were polished with a slurry of fine ferric oxide powder. The surface composition and structure were investigated by electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy (XPS). In the high pressure-polished surface, iron was non-uniformly distributed but oxygen was mostly uniformly distributed, while in a light pressure-polished surface, iron and oxygen were uniformly distributed though at lower and higher concentrations, respectively. EPMA state analysis and XPS suggested that the iron might exist as Fe^{2+} in the outermost surface, while it might be in a metallic state in the inner surface layer.

Key words : Titanium, Polishing, Surface composition

INTRODUCTION

Titanium is known to be a corrosion-resistant material and a promising biomaterial. It has been applied to dental implants and jaw reconstruction. It is believed that the composition, structure and physical properties of the surface film formed on titanium play important roles in interfacial phenomena such as corrosion1) and biotissue reactions2−4).

On the other hand, titanium is difficult to machine, because of its plasticity, low heat conductivity, and chemical reactivity at high temperatures. It is not easy to grind, abrade or polish. Although titanium in an ambient environment is stable due to the passive oxide film on its surface, abrasive grains mechanically destroy the film and directly contact the metal that has inherently high chemical affinity with most elements. Grains of most abrasive materials wear out chemically through the mechanism called "chemical wear or diffusion wear."

Some researchers5,6) have reported that high speed grinding results in both chemical wear of abrasive grains and burn, or discoloration and contamination of the surface, and that this tendency is intensified by heavy grinding loads. In other studies, titanium was abraded with abrasive papers of silicon carbide grit and the surface composition was analyzed by electron probe microanalysis (EPMA)7) and X-ray photoelectron spectroscopy (XPS)[8]. In spite of slow-speed abrasion under tap water cooling, the surface was observed to be contaminated by silicon and oxygen. When titanium embedded in a resin together with a stainless steel band for clipping was abraded, iron, chromium, nickel and calcium contaminated the surface more than silicon. The calcium came from a filler in the mold resin.

Such surface contamination could negatively influence titanium's resistance to *in-vivo* corrosion and biocompatibility. Therefore, it is important to elucidate the surface composition and structure of polished titanium for the efficient finishing of titanium appliance surfaces and for discussing reactions between biotissue and an implanted titanium surface.

The purpose of the present study was to investigate the surface composition and structure of titanium polished with aqueous slurry of fine ferric oxide powder. The results were compared to those of a similarly polished surface of silver-palladium-copper-gold alloy. EPMA and XPS were conducted for this purpose.

MATERIALS AND METHODS

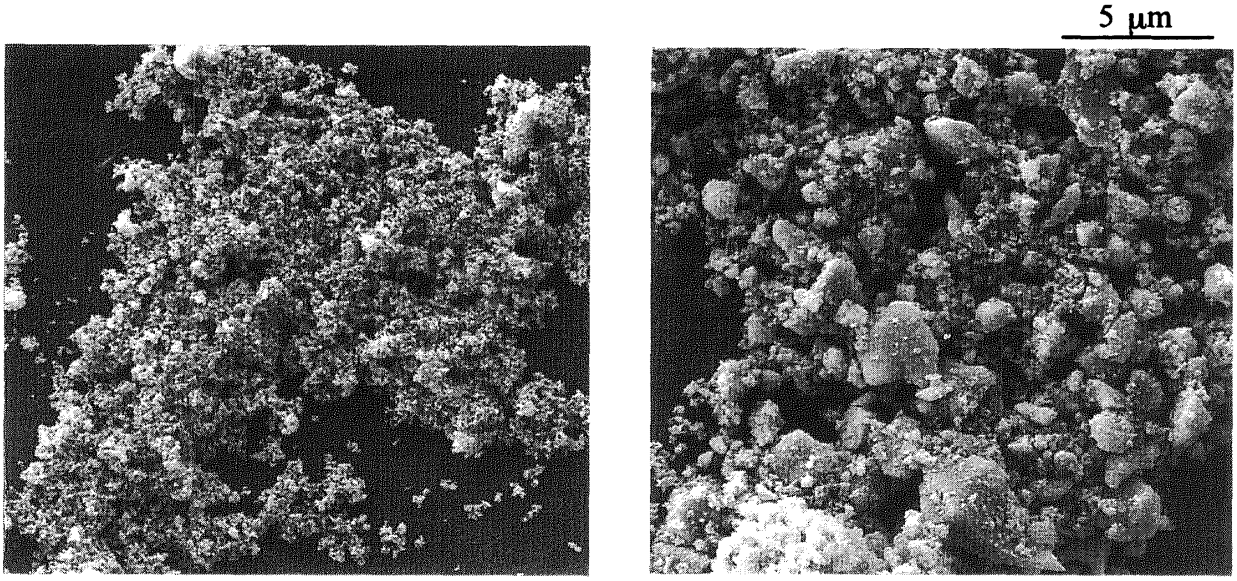
Preparation of specimens

Cast titanium plates of 1.4 mm thick were prepared according to a titanium casting system. A commercial titanium ingot (Pure Titanium A, Morita Co. Ltd., Kyoto, Japan) equivalent to class 2 of the Japanese Industrial Standard (JIS-H4600) was used. The plate size was 18 × 18 mm for EPMA and 8 × 8 mm for XPS.

Each specimen was adhered to a cylindrical resin block and set together with two dummy specimens for balancing in the specimen holder of a polishing machine (AUTOMAX, Refine Tec Co. Ltd., Yokohama, Japan) for metallurgical structure observation. The specimens were abraded with waterproof abrasive papers to #600 grit of silicon carbide under tap water cooling, and then polished with a buffing cloth on which aqueous slurry of fine ferric oxide powder (Iron oxide, Marumoto Co. Ltd., Tokyo, Japan) was supplied. Fig. 1 (a) shows a secondary electron image of this powder. The grain size was in sub-micron order.

Rotation speeds of the cloth and the specimen were 130 rpm and 50 rpm, respectively. Polishing pressure was controlled by adjusting the coil spring that presses the specimens on the cloth. A relatively high polishing pressure was exerted to one specimen for EPMA and one specimen for XPS, while a light pressure (a spring force of almost zero) to two specimens: one for comparison and the other for confirmation. The magnitude of the light pressure was estimated at about 75 gf/cm^2 from the weight of the specimen holder. The magnitude of the high pressure, if estimated, might be in the range of 300 to 600 gf/cm^2. Fresh buffing cloth was used for each specimen. The specimens were ultrasonically rinsed and finally cleaned in acetone.

A silver-palladium-copper-gold alloy, which was thought to have less or no reactivity with ferric oxide, was similarly investigated for comparison. One cast plate of 18 × 18 × 1.4 mm was prepared from a commercially available alloy (Castwell MC, GC Co. Ltd., Tokyo, Japan), according to the conventional process of dental casting.



(a) (b)

Fig. 1 Secondary electron images of two ferric oxide powders for polishing. Sub-micron powder (left) was used in this experiment.

The specimen was abraded and polished in the same manner as titanium, under light pressure.

Electron probe microanalysis

Using an electron probe microanalyzer equipped with a high-speed color mapping system (EPMA-8705-HII, Shimadzu Co. Ltd., Kyoto, Japan), distributions of titanium (or palladium), oxygen and iron in polished surfaces were analyzed in stage scan mode under the following conditions: accelerating voltage=15 kV, specimen current=$0.5 \mu A$, scanning step width=$1 \mu m$, and measuring time=70 ms/step. A spectroscopic crystal of lithium fluoride (LiF) was used to detect TiK_β and FeK_α. The layered structure analyzer (LSA, Shimadzu Co. Ltd., Kyoto, Japan), an artificially prepared spectroscopic crystal, which is 10 times or more sensitive as a spectroscopic crystal of rubidium acid phthalate (RAP), was used to detect OK_α.

To investigate the chemical states of oxygen and iron in polished surfaces, EPMA state analyses were conducted using the RAP crystal, which has relatively low sensitivity but high S/N ratio and high wave resolution. OK_α profiles from polished surfaces were compared with those from titania and ferric oxide as standard.

$FeL_{\alpha 1}$ and $FeL_{\beta 1}$ profiles from polished surfaces were compared with those from ferric oxide and pure iron as standard. In the state analysis of iron, however, one problem occurred, namely that the 7-th high order peak of TiK_α appeared and distorted the $FeL_{\alpha 1}$ profile, because the specimen was exposed to a high electron beam current for measuring the weak signal of FeL peaks. Thus, the X-ray signal was cut off through the pulse height selector. It was confirmed that the treated signal from titanium did not include the $TiK_{\alpha,n}=7$ peak. Then, the X-ray intensities in the range of 1.78~1.71 nm, covering the $FeL_{\alpha1}$ and $FeL_{\beta1}$ peak positions, were measured step by step, at intervals of 0.005 nm and a measuring time of 20 s/step.

In the case of the silver-palladium-copper-gold alloy, high-order characteristic X-rays from components constituting the alloy were also cut off through the pulse height selector, because they modified significantly OK_α, $FeL_{\alpha1}$ and $FeL_{\beta1}$ profiles. The state analyses were made by continuously scanning the RAP crystal at a speed of 0.02 nm/min.

Optical microscopy

The distribution of iron in the polished titanium surface was compared with the optical microstructure of a titanium casting. The specimen was abraded and polished in the same manner as described, and etched with 5 %HF-20%HNO_3 aqua. Optical microphotographs were taken.

X-ray photoelectron spectroscopy

The surface composition and structure of the high pressure-polished titanium surface were analyzed using an X-ray photoelectron spectroscopy analyzer (JPS-71XPS1, Japan Electron Optics Laboratory LTD., Japan). The X-ray source for excitation was MgK_α generated under a power of 10 kV and 20 mA. The analyzing chamber was held under a vacuum of 0.1μPa. The area of 6 mm in diameter was analyzed under the following conditions: scanning step width=0.1 eV and total measuring time=2.5 s/step. An analyzed area was pre-sputtered with gold for correction of the peak shift due to surface electron charge. Depth profiling was conducted by repetition of argon ion sputtering and subsequent measurement. The sputtering rate calibrated was about 12.8 nm/min for silica. The peak shifts of $Ti_{2p3/2}$, O_{1s} and $Fe_{2p3/2}$ were compared with those of standard substances published in the literature[1,9].

RESULTS AND DISCUSSION

High pressure-polished surface of titanium

Fig. 2 exemplifies the iron distribution map obtained by EPMA. For a quantitative evaluation, line profiles of TiK_β, OK_α and FeK_α are shown along the horizontal band indicated in the map. Letters, **A**, **B** and **C** indicate areas with low, higher and highest counts of FeK_α, respectively. Areas **A**, with 100 or less counts of FeK_α, showed a distribution pattern that corresponded to parallel lines (arrowheads in Fig. 3) in crystal grains surrounded by the serrated grain boundary (arrows in Fig. 3). In areas **B**, FeK_α was between 100 and 170, while in areas **C** it was far beyond the count of 170. According to the Japanese Industrial Standard (JIS-H4600), grade 2 titanium is allowed to include iron of less than 0.15%. The background count was about 70 near the FeK_α peak position. It was assumed, therefore, that iron in areas **A** was an impurity included in the titanium, while iron originating from the polishing material was added in areas **B** and **C**.

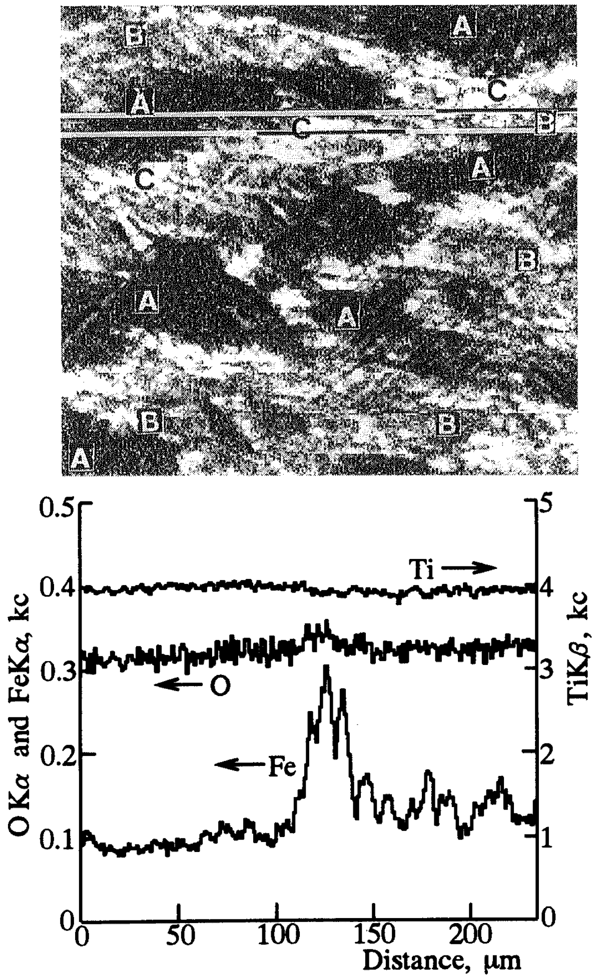


Fig. 2 Distributions of Ti, O and Fe in a high pressure-polished titanium surface.
Letters, A, B and C, indicate areas with low, higher and highest counts of FeK$_\alpha$, respectively. Line profiles of TiK$_\beta$, OK$_\alpha$ and FeK$_\alpha$ are shown along the horizontal band in the FeK$_\alpha$ map.

Regardless of the non-uniform distribution of iron, oxygen was almost uniformly distributed, with an average OK$_\alpha$ count of 320. If areas with high counts of FeK$_\alpha$ were contaminated by the ferric oxide, it is notable that little correspondence was found between the distributions of iron and oxygen. Titanium also was almost uniformly distributed, with an average TiK$_\beta$ count of 4,000. This uniform distribution of titanium implies that the absolute amount of iron was not so high in the polished surface.

Fig. 4 (a) exemplifies OK$_\alpha$ profiles from the high pressure-polished titanium surface, together with those of titania and ferric oxide as standard. Position **1** showed

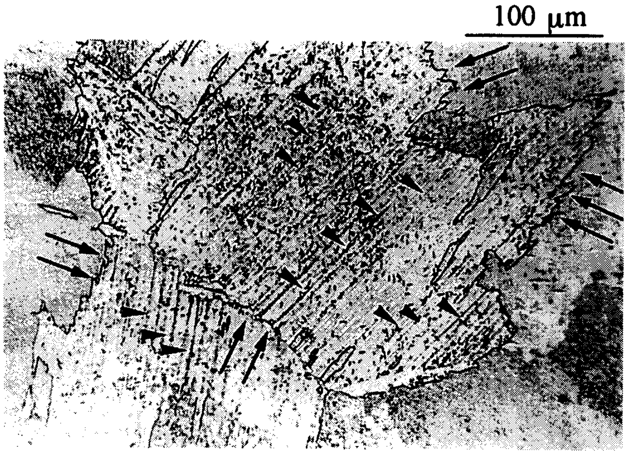


Fig. 3 Optical microphotograph of a titanium casting.
Arrows and arrowheads indicate serrated grain boundary and parallel lines in the crystal grain, respectively.

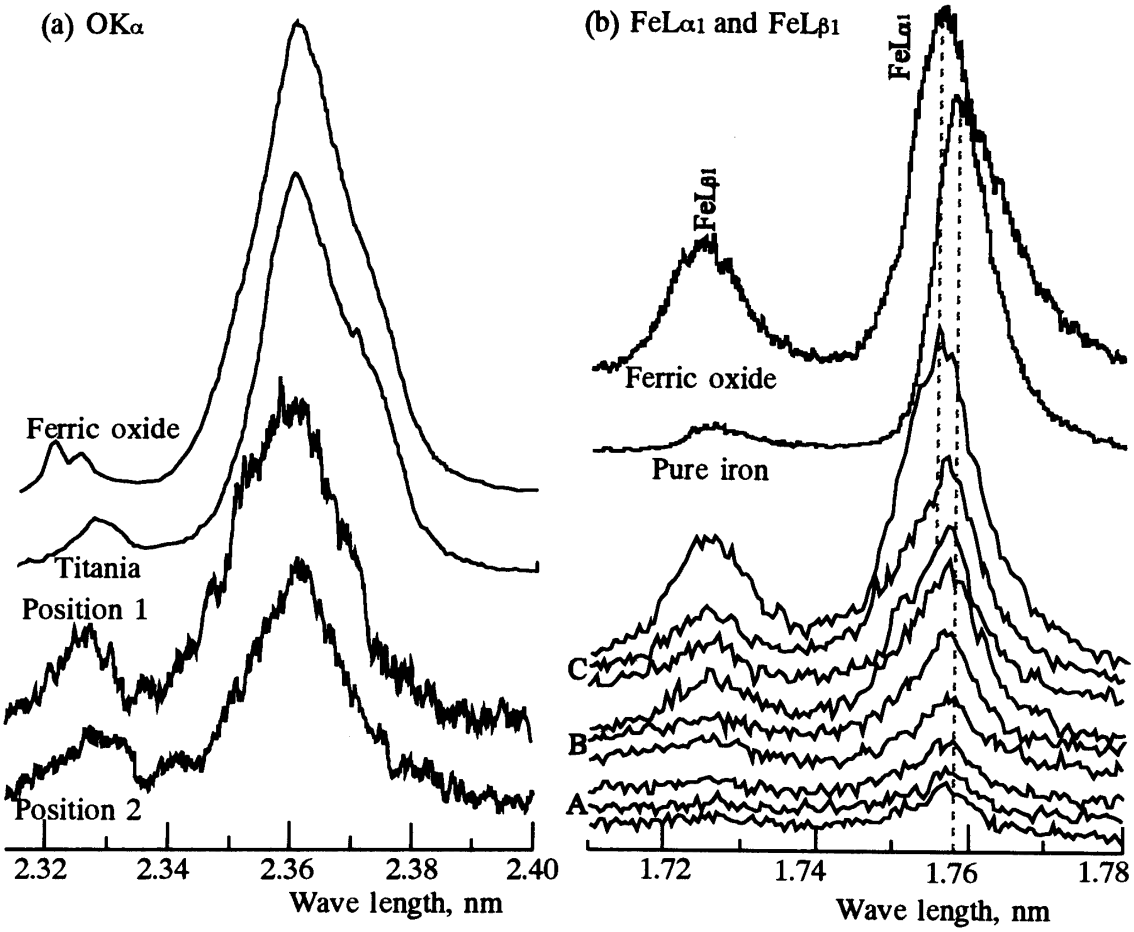


Fig. 4 EPMA state analyses of oxygen and iron in a high pressure-polished titanium surface.
Standard substances are titania and alumina for oxygen, and ferric oxide and pure iron for iron.

a very high count of FeK_{α}, while position **2** showed a relatively high count of FeK_{α}. OK_{α} profiles appeared to be similar to those from titania or ferric oxide. However, no detailed information was obtained, because of the small amounts of oxygen in the polished surface.

Fig. 4 (b) shows $FeL_{\alpha 1}$ and $FeL_{\beta 1}$ profiles from the high pressure-polished titanium surface, together with those from ferric oxide and pure iron as standard. Three profiles are drawn in each group, **A**, **B** and **C**, in which FeK_{α} intensity showed about 100 counts, about 140 counts, and counts above 170, respectively. In other words, each group corresponded quantitatively to areas **A**, **B** and **C** as described in Fig. 2.

It has been reported[10] that iron constitutes oxides such as FeO, Fe_3O_4 and Fe_2O_3, when the ratio of $FeL_{\beta 1}$ to $FeL_{\alpha 1}$ peak height is greater than 1/3, while it is of metallic component when the ratio is less than 1/5. With one exception, however, FeL peaks were weak and the ratio $L_{\beta 1}/L_{\alpha 1}$ could not be determined. On the other hand, it is known that the $FeL_{\alpha 1}$ peak of iron oxides shifts to the lower wave length side[11]. Thus, $L_{\alpha 1}$ peak shift was compared between the specimen and the standards.

At one point (group **C**) where the FeK_{α} count was highest in Fig. 4 (b), the appearance of the high $L_{\beta 1}$ peak showed that the iron constituted some iron oxide. Probably, the oxide comprised abrasive grains embedded in the polished surface. On the other hand, $L_{\alpha 1}$ peaks of the other 8 profiles deviated from their center to the higher wave length side, suggesting that the polished surface contained components of both iron oxides and metallic iron. These findings suggest that some abrasive grains were embedded in the polished surface and that the ferric oxide might become reduced during high pressure polishing.

Surface composition and structure of high pressure-polished titanium

To elucidate the surface composition and structure of the high pressure-polished titanium surface, XPS analysis was conducted. Fig. 5 shows the depth profiles of Fe_{2p}, O_{1s} and Ti_{2p}. Depth profiles of O_{1s} and Ti_{2p} were qualitatively similar to those shown by other researchers.

On the other hand, that which EPMA state analyses (Fig. 4 (b)) suggested became clear from the depth profiles of Fe_{2p}. Before the specimen was sputtered for 20 s, an $Fe_{2p3/2}$ peak corresponding to ferrous oxide was clearly observed. The peak corresponding to metallic iron appeared after the specimen was sputtered for 20 s. The peak reached maximum when sputtered for 50 s, and completely disappeared when sputtered for 250 s.

EPMA analysis (Fig. 2) and microstructure observation (Fig. 3) provided information from two kinds of iron; one is an impurity included in titanium and the other originates from the polishing material. When the specimen was sputtered for 250 s and 400 s, the $Fe_{2p3/2}$ peak disappeared. XPS could not detect iron as an impurity because of its low concentration. The iron might exist as Fe^{2+} (probably, $FeTiO_3$) in the outermost surface, while it might exist as metallic atom in the inner surface layer.

Concerning the above results, we must consider the report of Kim *et al.*[12] They

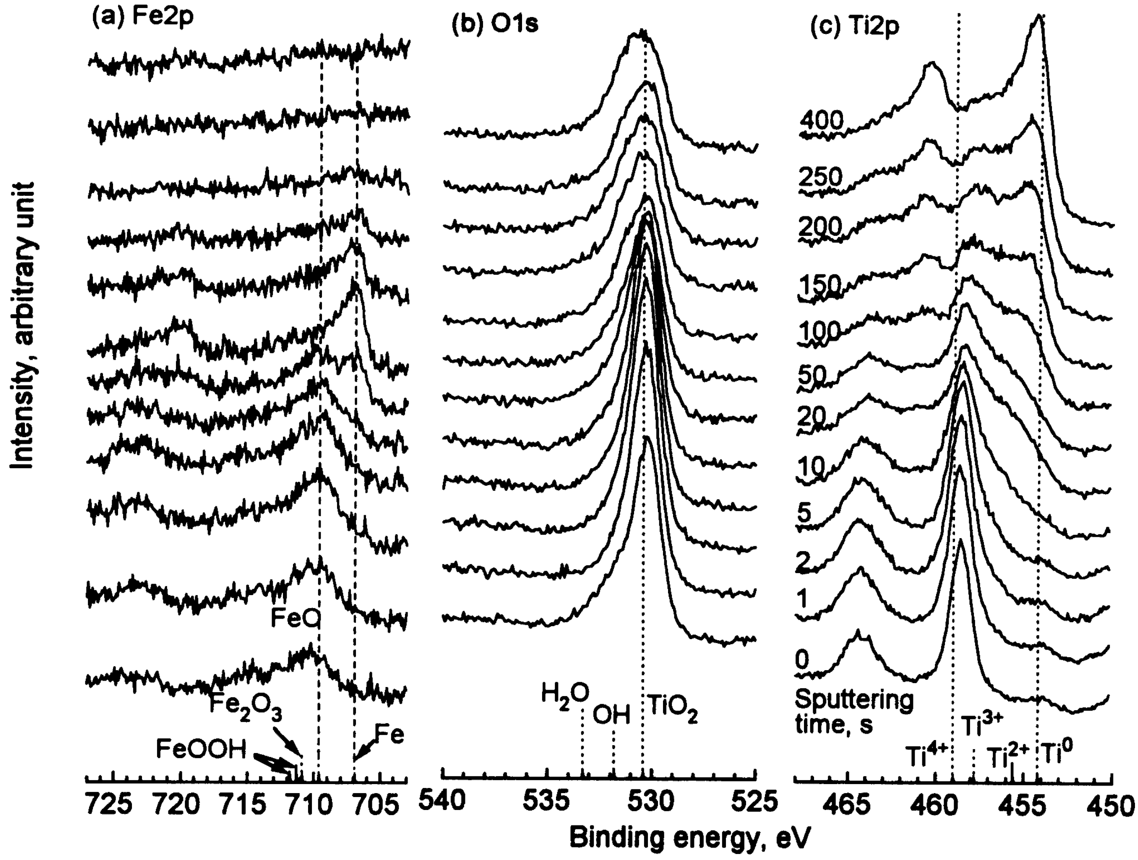


Fig. 5 XPS depth profiles of Ti_{2p}, O_{1s} and Fe_{2p} in a high pressure-polished titanium surface.
The positions of $Ti_{2p3/2}$ and O_{1s} peaks for standard substances were plotted from literature[1]. Those of $Fe_{2p3/2}$ peaks were plotted from literature[9].

found, without exception, that the behavior of oxides can be well predicted by the room temperature free energy of formation of the oxide, ΔG^0_f. All oxides with $-\Delta G^0_f$ below 60 kcal/mole were reduced by exposure to Ar^+ ions, while all those with $-\Delta G^0_f$ above 108 kcal/mole were stable to this exposure. $-\Delta G^0_f$ of ferrous oxide is 58 kcal/mole. Whether the oxide in the polished surface was FeO or $FeTiO_3$, it was partly reduced during argon ion sputtering. However, the peak of metallic iron appeared after short sputtering. In addition, EPMA state analyses also suggested the existence of metallic iron in the polished surface. Therefore, it is probable that Fe^{2+} changed to metallic iron during the polishing. The depth profiles of iron (Fig. 5 (a)) shows qualitatively the surface composition and structure in the polished titanium surface.

Polished surface of Ag-Pd-Cu-Au alloy

As a comparison, the light pressure-polished surface of a commercial silver-palladium-copper-gold alloy was investigated in the same manner as titanium. Fig. 6 exemplifies the line profiles of PdL_α, OK_α and FeK_α. Unlike the polished titanium

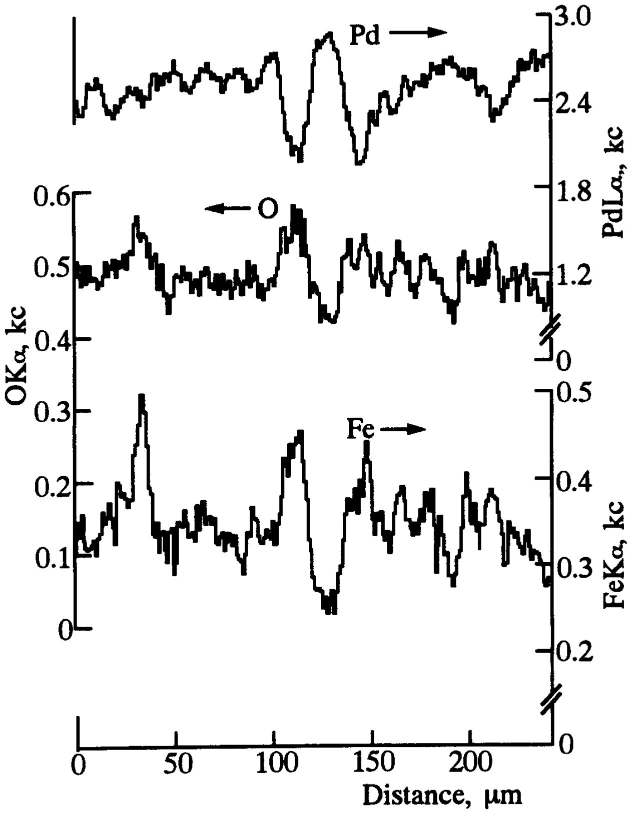


Fig. 6 Line profiles of PdLα, OKα and FeKα along a line in Ag-Pd-Cu-Au alloy surface polished with aqueous slurry of fine ferric oxide powder.

surface (Fig. 2), iron was non-uniformly distributed with close correspondence to oxygen and with reverse correspondence to palladium. Compared to the polished titanium surface, the intensities of OKα and FeKα were high, which were related to the high background level of X-rays from this alloy. The background counts were about 150 and 160 near the FeKα and OKα peak positions, respectively. It is clear, however, that the polishing material contaminated the entire polished surface, regardless of fluctuations in certain places.

EPMA state analyses were conducted for oxygen and iron at four points where the FeKα count was not so high. As exemplified in Fig. 7, the results suggested that the iron constituted an iron oxide. Probably, abrasive grains were embedded in the polished surface, without changing to metallic iron.

Polishing condition

Titanium is known to be difficult to machine. Many dental technicians have experienced some difficulty in obtaining mirror surface on titanium. Using the ferric oxide powder used in this experiment, we successfully finished titanium surfaces for metallurgic structure observation and EPMA analysis. However, all might not have gone

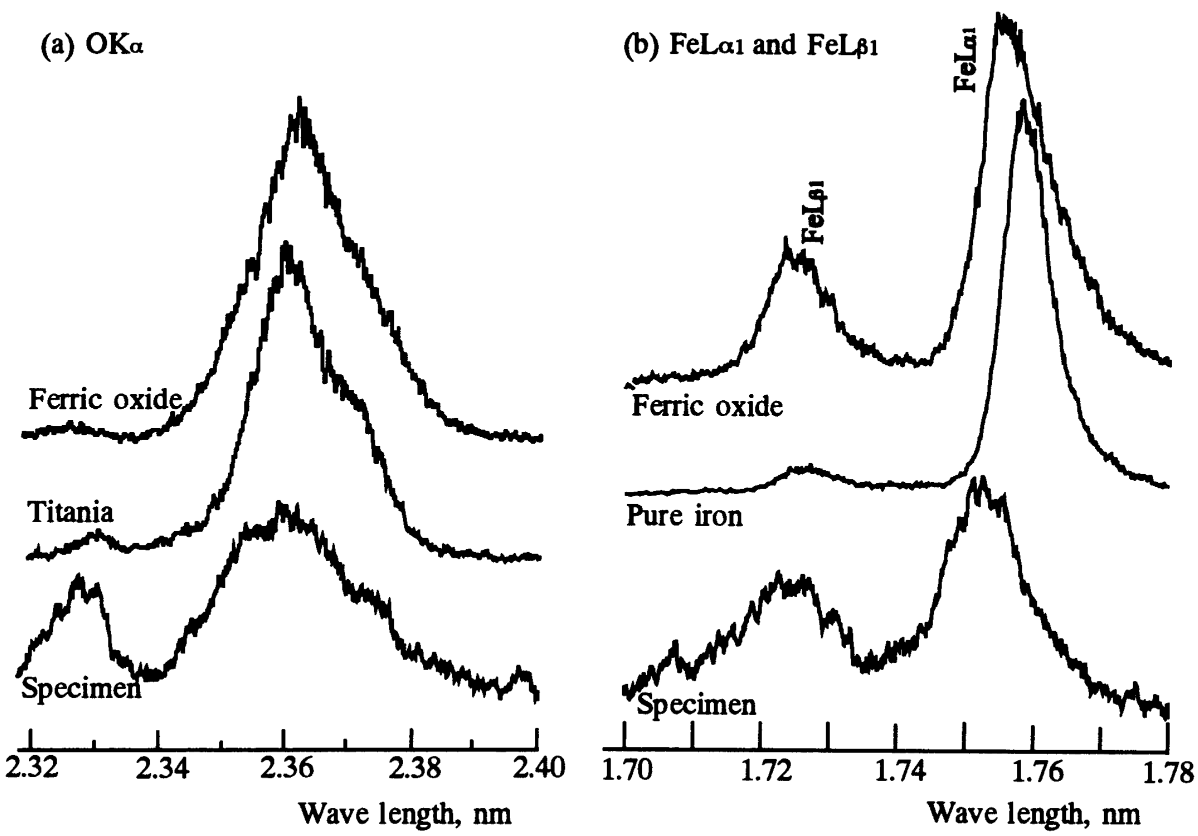


Fig. 7 EPMA state analyses of oxygen and iron in polished Ag-Pd-Cu-Au alloy surface.

well, even if ferric oxide powder was used as polishing material. The size of abrasive grains is an important factor.

The powder used in this experiment is on the left in Fig. 1. Compared with the powder on the right (nominally, a size of 3μm; iron oxide, #40-6445-016, BUEHLER, USA), the grain size shown on the left was very fine in sub-micron order, which might serve to successfully obtain a mirror surface of titanium. Coarser abrasive grains tend to form deeper scratches on the surface, to stick the surface, and to make the formation of a mirror surface difficult.

Another key point for obtaining a mirror surface on titanium is polishing pressure. The results shown in Figs. 2, 4 and 5 were obtained from the specimen polished under a higher pressure than usual. It is important to note that a light pressure (no additive pressure except for the weight of the specimen holder itself) has been usually used when specimens were prepared for various analyses. It takes a long time to reach the goal, but light pressure provides a better quality of polished surface. Fig. 8 exemplifies the line profiles of TiK$_\beta$, OK$_\alpha$ and FeK$_\alpha$ in a light pressure-polished surface of titanium. It is notable that iron was almost uniformly distributed with a lower than average FeK$_\alpha$ count of 100. Compared with high pressure (Fig. 2), light pressure decreased the amount of iron in the polished surface, while it increased somewhat the amount of oxygen (from 320 to 380 counts). A mirror surface was

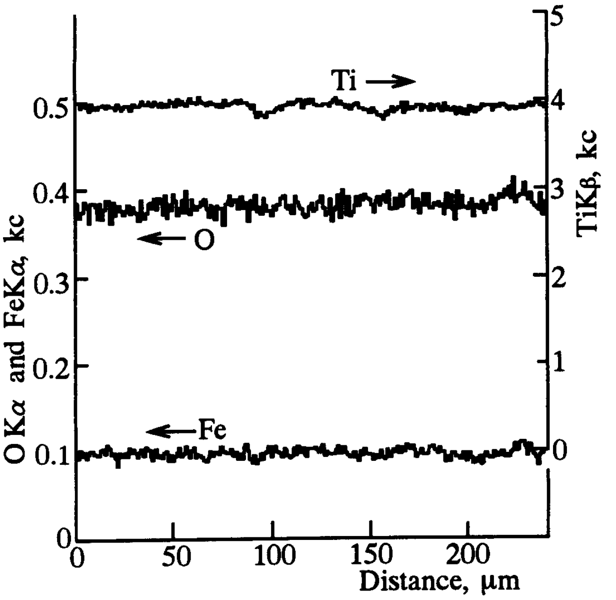


Fig. 8 Line profiles of TiK_{β}, OK_{α} and FeK_{α} in a low pressure-polished titanium surface using slurry of fine ferric oxide powder.

obtained, accompanied by less contamination from the polishing material. These results were confirmed using another specimen.

In conclusion, the titanium surface was contaminated by a small amount of iron when polished with aqueous slurry of fine ferric oxide powder under high pressure. The iron might constitute an oxide (probably, $FeTiO_3$) in the outermost surface and exist as metallic atoms in the inner surface layer. This behavior of iron was not found in the polished silver-palladium-copper-gold alloy. This difference between titanium and the alloy might be related not to the magnitude of polishing pressure but to the inherently high reactivity of titanium. Together with the magnitude of pressure, the size of abrasive grains is also related to the surface composition and structure of polished titanium.

Recently, Hirata *et al.*[13] reported that silica sol successfully provided a mirror surface on titanium. However, the reason why silica sol is effective in titanium polishing remains unclear. Why is it not so easy to obtain mirror surface? How do we polish titanium for efficient finishing? As an approach to this problem, the surface composition and structure of titanium polished with various polishing materials should be further investigated.

CONCLUSION

A commercial titanium and a silver-palladium-copper gold alloy were polished with aqueous slurry of fine ferric oxide powder.

In the polished surface of a silver-palladium-copper gold alloy, iron was non-uniformly distributed with a close correspondence to oxygen and with a reverse correspondence to palladium. Probably, the contamination reflected the embedding of abrasive grains into the polished surface.

In the high pressure-polished titanium surface, iron was non-uniformly distributed but oxygen was almost uniformly distributed, while in the light pressure-polished surface, iron and oxygen were uniformly distributed though at lower and higher concentrations, respectively. EPMA state analyses and the depth profiles of $Fe_{2p3/2}$ in XPS suggested that the iron originating from the polishing material might exist as Fe^{2+} in the outermost surface, while it might be in a metallic state in the inner surface layer.

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