

Chemical mechanical polishing of titanium with colloidal silica containing hydrogen peroxide — mirror polishing and surface properties

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Chemical mechanical polishing (CMP) of cpTi (Ti) was carried out using two types of slurries, acidic and basic colloidal silica containing H₂O₂ up to 3 wt%, to obtain flat and mirror-polished surfaces without any contaminated and reacted layers. Polishing behavior and surface properties were investigated using AFM, EPMA, and XPS. Weight loss of Ti polished by CMP using the basic slurry was larger than that using the acidic one, and surface roughness was less than 2 nm RMS when basic slurry containing 3 wt% H₂O₂ was used. Moreover, three kinds of chemical species, OH⁻, O²⁻, and H₂O, were detected on the Ti surfaces polished by CMP using these slurries. Results of this study showed that CMP using colloidal silica containing H₂O₂ successfully created a mirror-polished surface without contaminated and reacted layers.

Key words: Chemical mechanical polishing, Titanium, XPS

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INTRODUCTION

Titanium has been widely used for making dental prostheses, dental implants and bone plates due to its excellent biocompatibility¹⁻³. The excellent biocompatibility of Ti is a function of its surface characteristics⁴. In other words, the characteristics of the Ti surface play a key role in its biocompatibility. Most of the surfaces of cast and polished Ti have a reactive and contaminated layer⁵⁻⁹. It was assumed that these layers which form on the Ti surface influence the biocompatibility and mechanical properties.

For this reason, it is necessary to produce a clean Ti surface without reactive and contaminated layers. We have proposed an electrochemical polishing method to prepare clean Ti surfaces¹⁰. When this method was applied to Ti polishing, no elements responsible for causing contamination were detected by electron probe microanalysis (EPMA)¹⁰. In light of the result obtained¹⁰, this method showed itself to be an effective surface treatment for Ti to render it to be more biocompatible. However, the polished Ti surface was colored golden due to a thick oxide film formed by anodic oxidation.

Morita¹¹ had succeeded in electropolishing — not large Ti plates — but small ones using a non-aqueous electrolyte. However, the polished Ti surface was fogged up when the electrolyte contained water. Therefore, chemical mechanical polishing (CMP) was applied to the Ti plates to obtain a metallic luster. As the name implies, CMP involves both chemical

and mechanical actions that lead to removal from the surface layer and planarization at the same time¹². Of late, CMP has emerged as a key semiconductor polishing technology for achieving full global planarization¹³.

To study the optimal CMP conditions that will solve the drawbacks of electrochemical polishing and electropolishing as mentioned above, CMP behavior and surface properties for Ti using colloidal silica slurries containing H₂O₂ with different pH values were investigated.

MATERIALS AND METHODS

Preparation of specimens and CMP

Titanium ingots, 16 mm in diameter (equivalent to JIS Class 2; T-Alloy M, GC Corp., Tokyo, Japan), were abraded under tap water using an automatic polisher (Auto Max, RefinTech, Yokohama, Japan). The polishing disk of the automatic polisher rotated at a speed of 130 rpm, and the Ti ingots were moved in a planetary fashion at 50 rpm on the polishing disk. A #800 SiC waterproof paper was used for the final polishing of the Ti ingots. These specimens were used for the CMP.

Colloidal silica slurries for the CMP were prepared as follows. A colloidal silica slurry (MasterMet 2, Buehler, IL, USA) with a pH of 9.8 and mean grain size of 0.06 μm was termed the basic colloidal silica (BCS). For the colloidal silica with a pH of 3.2, it was adjusted using H₃PO₄ and NH₄H₂PO₄ solutions and was called the acidic colloidal silica (ACS). Thereafter, colloidal silica

slurries containing H₂O₂ of 0.3, 0.9, 1.5, 2.1, and 3 wt% were prepared for the CMP. In particular, BCS and ACS containing 3 wt% H₂O₂ were specifically termed as 3BCS and 3ACS respectively.

CMP was performed using the automatic polisher for 15 minutes under a polishing pressure of 1 kg/cm², while each slurry prepared as mentioned above was dropped on a buffing cloth (Chemomet I, Buehler, IL, USA). The specimens were ultrasonically cleaned in acetone for 5 minutes after CMP and then dried by blowing air.

Weight loss of the specimens after CMP

Each specimen's weight was measured with a chemical balance (Type L, Shimadzu, Kyoto, Japan) after the specimen was sufficiently dried. Difference in weight of the specimen before and after CMP was defined as the weight loss. Five specimens were tested.

Surface roughness measured by AFM

A commercial atomic force microscope (AFM) (JSPM-4210, JEOL, Tokyo, Japan) was used to perform the surface analysis of the specimens after CMP. Images of a 15×15 μm² scan were taken using a very fine tip (radius < 80 nm) for the probe. Five lines were randomly drawn on the AFM image obtained by an imaging program (WinSP, JEOL, Tokyo, Japan) for surface roughness analysis, and root mean square (RMS) value was calculated for each line. The average of these RMS values thus represented the average value of the specimen (n=7).

Oxygen mapping on the specimens by EPMA

Secondary electron (SE) images of the specimens were observed by EPMA (EPMA-8705-HII, Shimadzu, Kyoto, Japan) to study the morphology of the specimens. An oxygen mapping (O Kα) image was taken on the same area of each SE image to compare the surface morphologies in terms of chemical composition. Analysis conditions were as follows: accelerating voltage at 15 kV, specimen current at 0.5 μA, scanning step size at 1 μm, and sampling time at 70 ms/step. The location of an O Kα profiling was indicated by a line on the corresponding SE image.

Chemical analysis of polished specimen surface by XPS

The high-resolution, narrow O 1s spectra were recorded by X-ray photoelectron spectroscopy (XPS) (Quantum 2000, ULVAC-PHI Inc., Chigasaki, Japan) using an angle-resolved method to deduce the composition profile on the polished Ti surface. Range of the angles taken was 5–45 degrees. A monochromated Al Kα X-radiation was used at a power of 2.5 W and at an accelerating voltage of 15 kV. To

neutralize the surface charges caused by irradiation, a flood gun was operated during the analysis. Base pressure during analysis was 10.67 μPa and analysis area was set at 10 μm in diameter.

Thickness of the oxide film formed on the specimen polished by CMP using either ACS, BCS, 3ACS, or 3BCS was investigated using the conventional XPS method, whereby high-resolution, narrow spectra (O 1s and Ti 2p) for the as-received conditions and after applying sputtering with an Ar beam at time intervals, were recorded. To this end, the O 1s intensity was normalized to estimate the oxide film thickness. Sputtering time required to halve the normalized peak height of O 1s was obtained, and film thickness was calculated on the basis of the sputtering rate of TiO₂. A half mirror for a laser diffraction, which was composed of interlaminated thin films of TiO₂ and SiO₂ of known thicknesses, was sputtered under the same conditions as the specimen. The sputtering rate of TiO₂ obtained was 0.58 nm/min.

Statistical analysis

All data for weight loss and surface roughness were analyzed by two-way analysis of variance. The main effects and interactions of two factors, namely slurry pH and H₂O₂ concentration, were evaluated for statistical significance of the differences among the data.

RESULTS

Effects of pH and H₂O₂ on weight loss

The relationship between H₂O₂ concentration and weight loss is shown in Fig. 1. According to multiple analysis of variance, the effects H₂O₂ concentration and slurry pH on weight loss were highly significant (p<0.01). No interaction was observed among the specimens.

Effects of pH and H₂O₂ on surface roughness

In Fig. 2, we plot the relationship between slurry pH and surface roughness RMS against the concentration of H₂O₂. Surface roughness gradually decreased as the concentration of H₂O₂ increased, independent of slurry pH. According to two-way analysis of variance, an interaction was observed among the specimens.

Elemental analysis of the polished surfaces by EPMA

Figure 3 shows the SE images and O Kα line profiles of the specimens which were processed with ACS, 3ACS, BCS, and 3BCS. The SE images of the specimens showed a metal structure related to the Ti grain. In particular, grain boundaries were vividly observed in 3BCS.

Average intensity of the O Kα signal of ACS-

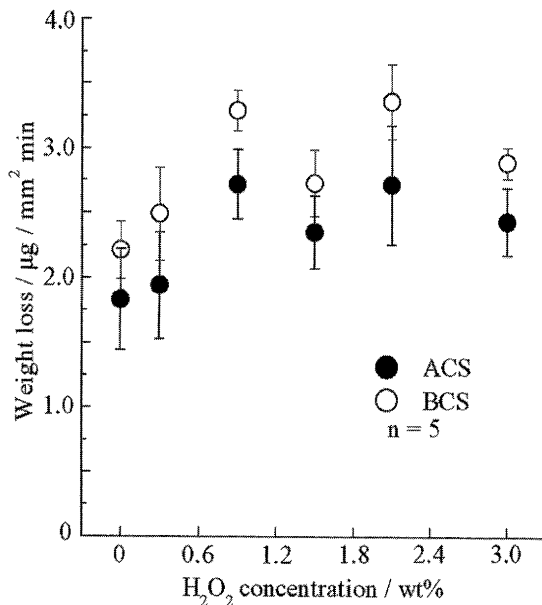


Fig. 1 Relationship between weight loss and the concentration of H_2O_2 added to the slurry. ACS: colloidal silica, pH 3.2; BCS: colloidal silica, pH 9.8.

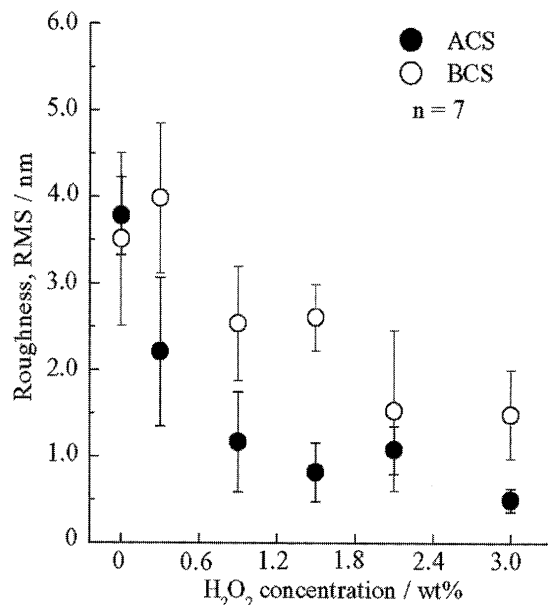


Fig. 2 Relationship between surface roughness and the concentration of H_2O_2 added to the slurry. ACS: colloidal silica, pH 3.2; BCS: colloidal silica, pH 9.8.

treated surface was the same as that of BCS-treated one. On the other hand, the average intensity of the O $K\alpha$ signal of 3ACS was about 25% higher than that of ACS. Similarly, the average O $K\alpha$ intensity of 3BCS was about 50% higher than that of BCS.

Chemical species on the polished surfaces and oxide film thickness

Figure 4 shows a typical Ti 2p spectrum for the polished specimen (prior to sputtering). It indicated a prominent Ti $2p_{3/2}$ peak at about 459.3 eV. According to published literature¹⁴, the binding energy of Ti $2p_{3/2}$ peak conformed to that of Ti in TiO_2 .

According to the O 1s spectrum obtained from the specimen, the main chemical species were postulated to be O^{2-} , OH^- , and H_2O . The O 1s peak was deconvoluted into three components, namely O^{2-} , OH^- , and H_2O peaks (Fig. 5). The binding energy values corresponding to these peaks were 530.3, 532.0, and 533.2 eV respectively¹⁵. The proportion of each chemical species was calculated on the basis of the area ratio as shown in Fig. 6. The proportion of O^{2-} in all specimens increased as the angle increased from low to high. On the contrary, the proportion of [H_2O and OH^-] decreased as the angle increased from low to high. In particular, a large proportion of H_2O on the outermost surface (5°) of 3ACS was a striking feature in comparison to the other conditions.

To calculate the thickness of the oxide film

formed on the specimen treated with either ACS, 3ACS, BCS, or 3BCS, a relationship between the sputtering time and normalized intensity of O 1s is shown in Fig. 7. Oxide film thickness was determined from the sputtering time at half of the normalized intensity¹⁶. As the sputtering time of the specimens treated with ACS and BCS was about 10 minutes, the film thickness of these specimens was estimated to be 5.8 nm. As for 3ACS and 3BCS, the thicknesses of their oxide films were estimated to be 6.7 nm and 7.7 nm respectively.

DISCUSSION

CMP is a process that combines both mechanical and chemical polishing¹². The mechanical polishing thereof planarizes a specimen surface by the action of the abrasive grains. As for the function of chemical polishing, it dissolves the metal surface by an acid-base or redox reaction. Kaufman *et al.*¹⁷ studied the CMP of W with slurries containing silica or alumina abrasive and oxidant $\text{K}_3\text{Fe}(\text{CN})_6$ below a pH of 6.5. They suggested that WO_3 was formed on the W surface by the oxidant and that the oxide film played an important role in creating a mirror finish. In our study, the CMP yielded a TiO_2 film on the Ti surface that was highly specular and which appeared scratch-free to the human eye.

Chiu *et al.*¹⁸ reported on the effects of H_2O_2 concentration and pH value on CMP for Ti using a potentiodynamic scan. It was found that a higher

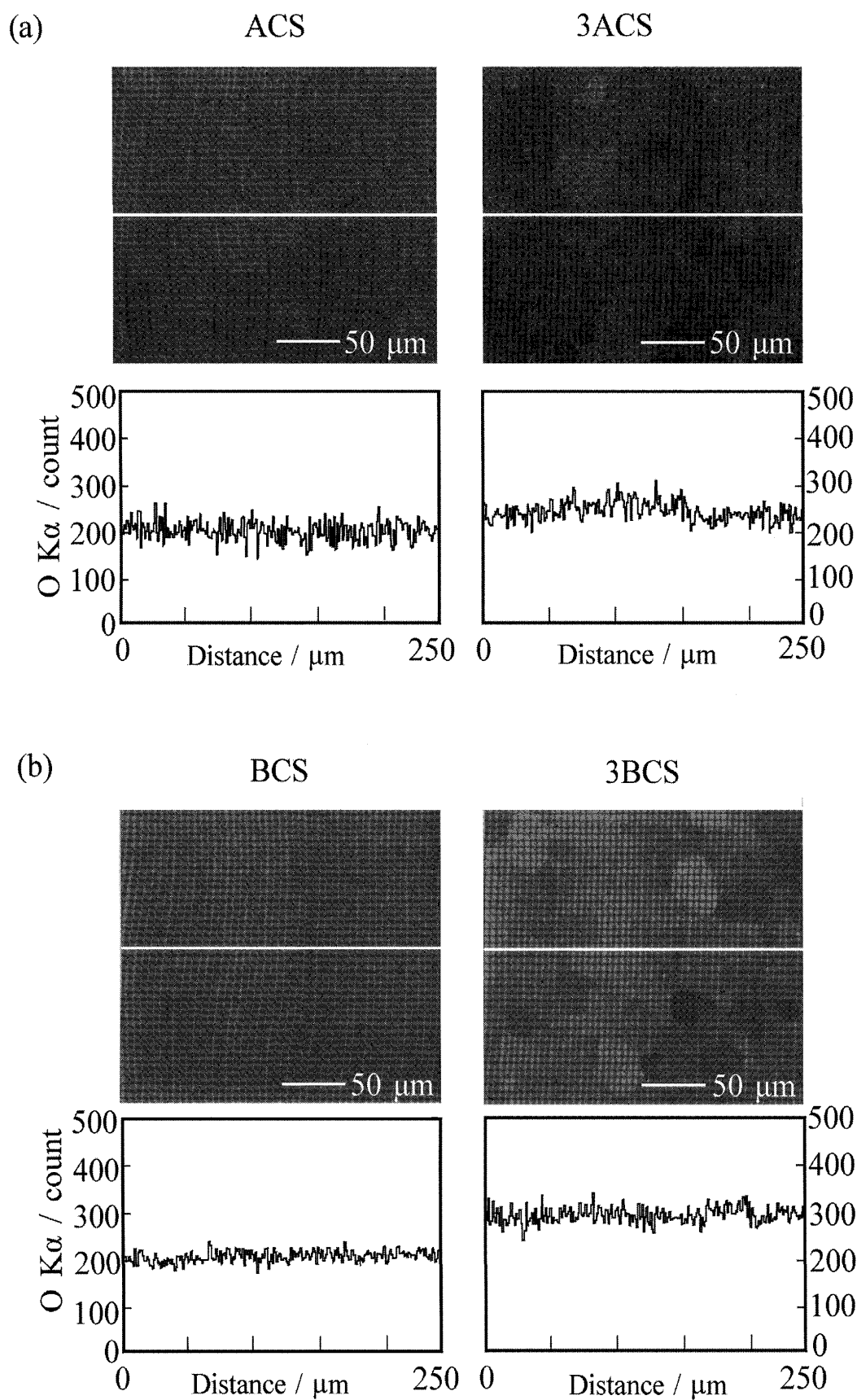


Fig. 3 SE images of the surfaces polished with CMP and O K α line profiles. The location of an O K α profiling was indicated by a line on the corresponding SE image.

- (a) Treated with colloidal silica slurry of pH 3.2 (ACS) and ACS containing 3 wt% H₂O₂ (3ACS).
 (b) Treated with colloidal silica slurry of pH 9.8 (BCS) and BCS containing 3 wt% H₂O₂ (3BCS).

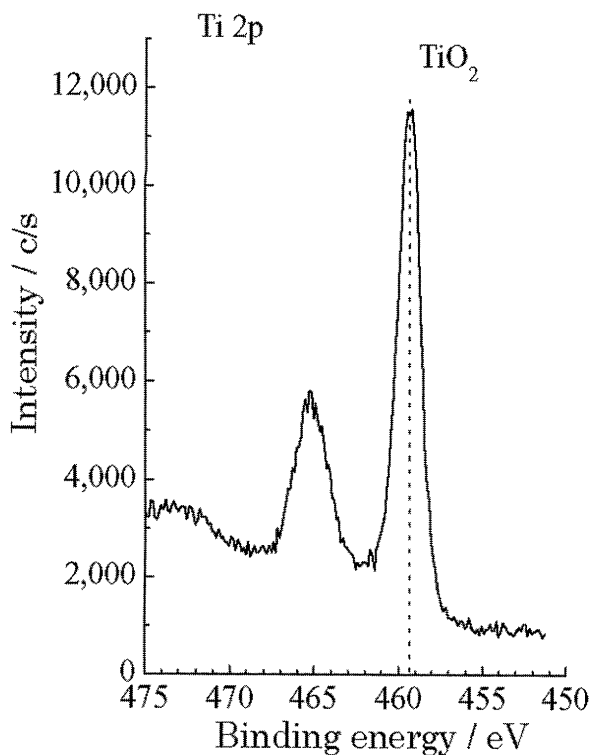


Fig. 4 A typical Ti 2p spectrum for the polished specimen (prior to sputtering).

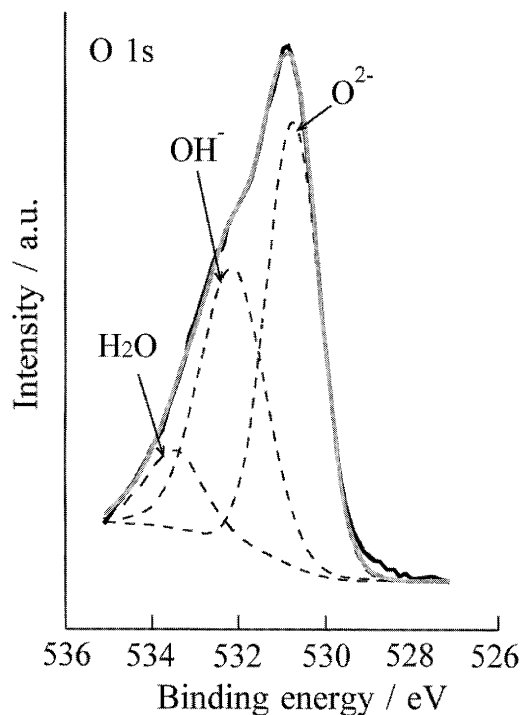


Fig. 5 O 1s XPS peaks of oxide-covered Ti (prior to sputtering). The reference binding energies used in resolving the O 1s peaks were 530.3 eV for O^{2-} , 532.0 eV for M-OH, and 533.2 eV for M-H₂O.

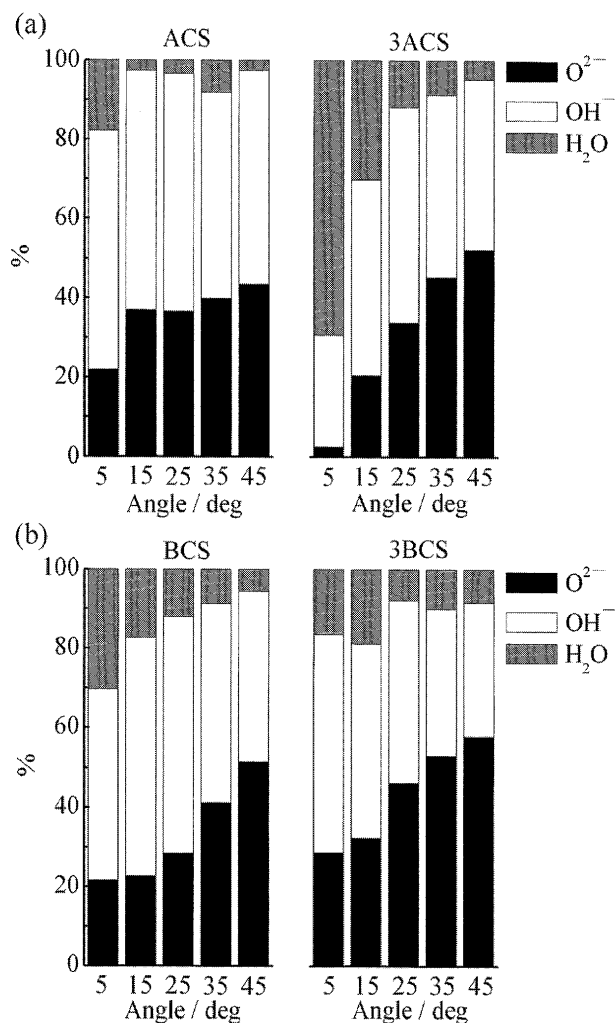


Fig. 6 Ratios of the chemical species which were analyzed using the XPS angle-resolved method, on the polished surfaces of:

- ACS: Colloidal silica slurry of pH 3.2;
- 3ACS: ACS slurry containing 3 wt% H₂O₂;
- BCS: Colloidal silica slurry of pH 9.8;
- 3BCS: BCS slurry containing 3 wt% H₂O₂.

H₂O₂ concentration, up to 6 vol%, resulted in higher Ti oxidation rate and increased removal rate. Similarly, higher pH values—at a range of 2 to 6—resulted in increased Ti removal rate. In our study, similar results were obtained in that weight loss was larger with the slurry containing H₂O₂ as much as 3 wt%. Therefore, the chemical action of H₂O₂ significantly affected weight loss.

The chemical action of H₂O₂ demonstrated strong oxidation in both acidic and basic solutions¹⁹. Thus, H₂O₂ reacted with fresh Ti exposed by the abrasive particles, and then TiO₂ was formed by the following reaction: $Ti + 2H_2O_2 \rightarrow TiO_2 + 2H_2O$. In other words, H₂O₂ promoted the oxidation of Ti in both acidic and basic solutions. Chiu *et al.*¹⁸ reported that the

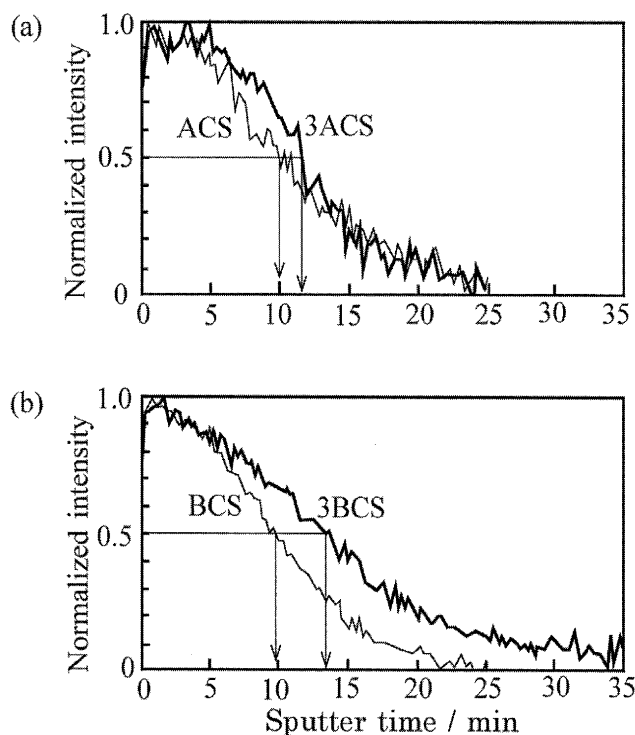


Fig. 7 Relationship between sputtering time and the intensity of normalized O 1s after CMP for:

- (a) ACS: colloidal silica slurry of pH 3.2; 3ACS: ACS slurry containing 3 wt% H_2O_2 .
 (b) BCS: colloidal silica slurry of pH 9.8; 3BCS: BCS slurry containing 3 wt% H_2O_2 .

dissolution reaction of TiO_2 ($\text{TiO}_2 + \text{OH}^- \rightarrow \text{HTiO}_3^-$) with increasing pH values occurred when TiO_2 reacted in the presence of H_2O_2 . In our study, the dissolution reaction might have occurred during the CMP which used H_2O_2 -containing slurries. In this light, it was conceivable that weight loss might depend on both TiO_2 removal and the dissolution of TiO_2 in the presence of H_2O_2 .

The effects of slurry pH and H_2O_2 concentration on surface roughness could not be interpreted in a straightforward and simplistic manner as an interaction was observed between the specimens. Although the interaction was highly significant, it was necessary to discuss the main effect in the event of a large variance for the main effect²⁰⁾. Regardless of slurry pH, the surface roughness of the specimens polished by CMP became smaller with increasing H_2O_2 concentration. Some chemical actions to cause the planarization, like dissolution and hydration, might also be initiated by H_2O_2 during CMP.

According to the EPMA analysis results on the average intensity of O $K\alpha$ signals, the oxidation of Ti was promoted by the combined effects of slurry pH and H_2O_2 concentration. Thickness of the oxide film, as estimated by XPS, was almost the same with both

ACS and BCS—that is, without H_2O_2 . On the contrary, film thickness of the specimen treated with 3BCS was larger than that treated with 3ACS. These results indicated that the oxidation of Ti might be stronger at a basic pH. Chathapuram *et al.*²¹⁾ reported that the forming rate of TiO_2 was faster compared to the removal rate, and suggested that the Ti surface was always covered with a thin oxide film during CMP. Under our CMP conditions, a thin oxide film was indeed formed on the specimen. Thus, the polished surface had no reacted layer. Most probably, the thin oxide film had resulted in less reaction between the abrasive and Ti.

By means of XPS angle resolution measurement, the ratio of water and hydroxide ion species became lower with increasing XPS angle, while that of O^{2-} species became larger. The O^{2-} species originated from TiO_2 based on the XPS data. However, the outermost surface treated with 3ACS had abundant H_2O species. Besides the adsorbed water, the reaction product²²⁾ having functional H_2O groups, e.g., $(\text{Ti}(\text{H}_2\text{O})_6)^{3+}$, might be formed by the reaction between the slurry and Ti or TiO_2 . In contrast, the other specimens had a relatively large amount of OH^- . It was important to investigate and examine the chemical species on the outermost surface because the chemical species reacts with the surrounding chemical species. On this note, Tanaka *et al.*²³⁾ indicated that the OH^- group in the oxide film contributed to the formation of calcium phosphate compounds. Consequently, the properties of Ti surface polished by CMP might contribute to biocompatibility.

CONCLUSIONS

CMP of Ti was carried out using acidic and basic colloidal silica slurries containing H_2O_2 . The effects of slurry pH and H_2O_2 concentration on polishing behavior and surface properties were then investigated. Within the limitations of this experiment, the polished specimen was found to be highly specular and the weight loss of Ti using the basic slurry was larger than that using the acidic one. On the other hand, regardless of slurry pH, surface roughness became smaller with increasing H_2O_2 concentration. The chemical species on the surface polished by CMP using colloidal silica slurry containing H_2O_2 were primarily OH^- , H_2O , and O^{2-} . Therefore, a mirror-polished Ti surface without reacted layer was created by means of CMP using a colloidal silica slurry containing H_2O_2 .

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