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SURFACE TREATMENT AND EXAMINATION OF GRADE 2 AND GRADE 5 TITANIUM

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Abstract. Surface characteristics play an important role in the implant-bone integration that is required for the long-term reliability of dental and orthopedic implants. In this paper, we investigate the effect of acid etching on the mass reduction and roughness of grade 2 and grade 5 Ti under controlled experimental conditions. Three different etching compounds were investigated: 30% HCl, 85% H_3PO_4 and the compound of 30% $(COOH)_2 \times 2H_2O$ and 30% H_2O_2 in various treatment intervals under controlled temperature. Stereo microscopy, scanning electron microscopy, roughness and weight measurements were carried out on the samples. We found that neither 85% H_3PO_4 nor the compound of 30% $(COOH)_2 \times 2H_2O$ and 30% H_2O_2 were able to remove the machining marks from the surface of Ti discs in our experimental setting. On the other hand, etching in 30% HCl yielded even surfaces both on Ti grade 2 and 5 discs. We also found that etching at higher temperatures in 30% HCl resulted in significant mass loss.

Keywords: titanium, chemical etching, mass reduction, roughness.

1. Introduction

Pure titanium and titanium alloys are well-established standard materials of dental and orthopedic implants because of their favorable mechanical strength, chemical stability and biocompatibility [1]. Nowadays, the most frequently used pure titanium is identified as "commercially pure" (CP) grade 2 and 4. However, a titanium-vanadium-aluminum alloy, reported as grade 5 or labeled as Ti6Al4V, is also commonly used. The integration of titanium dental implants with the surrounding bone tissue (osseointegration) is critical to ensure the long-term survival and functionality of the implants [2]. The concept of osseointegration was discovered by Brånemark and his co-workers. Their research has had a dramatic influence on the design of implants and consequently the clinical outcome of dental implant surgeries [3]. The first generation of successfully applied titanium implants had simple machined surfaces. Since then, implant surfaces have long been recognized to play an important role in molecular interactions, cellular response and osseointegration. Therefore, tremendous scientific efforts have been focused on the development of implants with surfaces that have the capability of accelerating the osseointegration and improving the long-term survival of the implants. For that purpose, various methods have been developed during the last 20 years, such as sandblasting, acid etching, bioactive coatings, anodization and, more recently, laser modification of surfaces [4–6]. These implants have been extensively investigated in *in vivo* experiments, including long-term clinical studies and experimental histological and biomechanical evaluation in animal models [7].

Titanium and titanium alloys are prone to develop a superficial oxide layer upon contact with oxidants [8]. The quality of the oxide layer may profoundly affect the biological behavior of titanium implants. The mechanical properties of the oxide layer, such as the thickness, texture and roughness are known as the most important parameters that may affect the rate of osseointegration and the biomechanical properties of the devices [9]. Several types of surface treatment methods have been proposed in the scientific literature, including mechanical and chemical procedures to improve the osseointegration ability of dental implants. However, usually these publications do not disclose details about the effect of treatment parameters on the mechanical properties of titanium, but rather focus on the optimization of biological properties of the oxide layer [7–10].

2. Aim of Experiment

In this paper, we focus our attention on the effect of acid etching on the mass reduction, surface texture and roughness of Ti grade 2 and Ti grade 5 samples under controlled experimental conditions.

3. Experiment

Titanium discs of 2 mm thickness and 14 mm in diameter were cut from grade 2 and grade 5 rods with a turning machine. The weight, roughness and surface texture of the discs were recorded after machining.

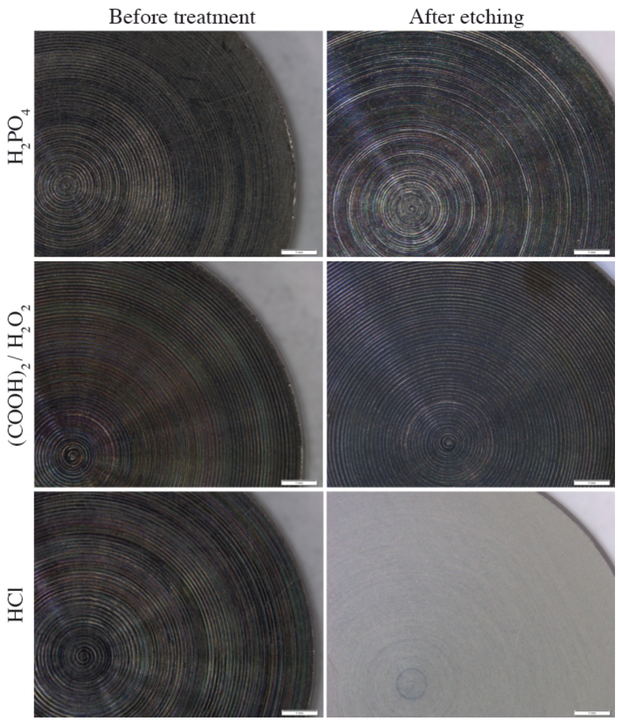

Figure 1. Stereo microscopic images of titanium discs before and after etching in H_3PO_4, in the compound of $(COOH)_2 \times 2H_2O$ and H_2O_2 and in 30% HCl.

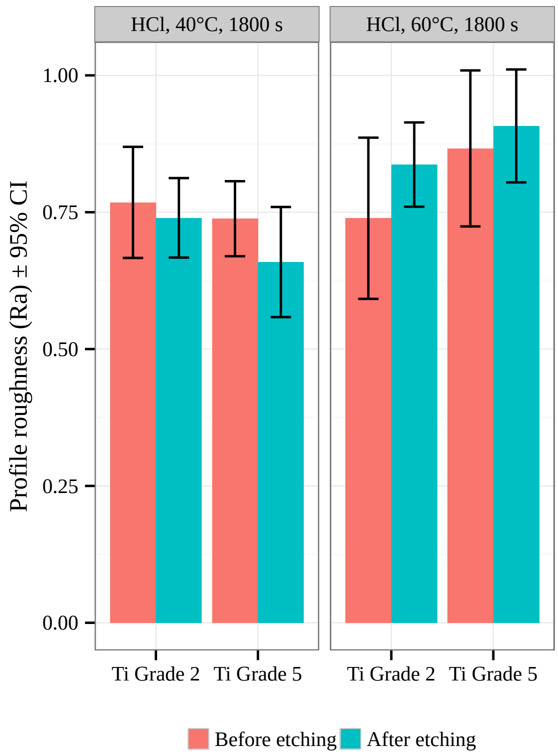

Figure 2. Mean profile roughness values and their 95% CIs for Ti grade 2 and Ti grade 5 discs before and after etching in 30% HCl at 40°C for 1800 seconds and at 60°C for the same duration.

3.1. Chemical Etching

After turning, 54 pieces of Ti grade 2 and 54 pieces of Ti grade 5 discs were subjected to acid etching. We investigated the effect of three different acids: 30% hydrochloric acid (HCl), 85% phosphoric acid (H_3PO_4), and the compound of 30% oxalic acid ($(COOH)_2 \times 2H_2O$) and 30% hydrogen peroxide (H_2O_2). The etching intervals were 10, 600, 1800, 3600, 5400 and 7200 seconds at three temperatures: 20°C, 40°C and 60°C.

3.2. Weight Measurement

The weight of the samples was measured (DENVER Instrument APX-200, New York, United States) after each etching interval. The differences in the weight of the titanium discs measured before and after chemical etching were calculated and plotted.

3.3. Microscopy

Stereo microscopic (Olympus SZX16, Pennsylvania, United States) images were taken of the titanium discs after each etching interval in each experimental group in order to record the surface texture of the samples (Figure 1). Only those samples were further investigated by scanning electron microscopy (Philips XL 30, Zagreb, Croatia) where the machining marks disappeared from the surface of the discs (see HCl row on Figure 1).

3.4. Roughness Measurement

Five discs were selected from each experimental group and three measurements were performed on each disc. Profile roughness (Ra) measurements (Mitutoyo Surftest 211) were performed along 3 radial lines in 120°increments from the outer edge towards the center of each disc.

4. Results and Discussion

The stereo microscopic images showed that machining marks were visible on the surface of titanium discs with width of 15–20 µm (Figure 1). After etching either in 85% of H_3PO_4 or in the compound of 30% of $(COOH)_2$ x $2H_2O$ and 30% H_2O_2 the surface morphology of Ti grade 2 and Ti grade 5 discs was similar to the untreated surface meaning that the machining marks remained visible even after the 7200 second treatment (top and middle rows of Figure 1). On the other hand, the etching in 30% HCl markedly reduced the unevenness of the surfaces both on the Ti grade 2 and the Ti grade 5 discs (bottom row on Figure 1). Thus, only HCl etched titanium discs were subjected to further investigations.

Concerning the treatment parameters, such as time and temperature, the Ti grade 2 discs that were treated in HCl at 40°C for 1800 seconds and those that were treated in HCl at 60°C for 1800 seconds showed even surface patterns (Figure 3). However, we found a considerable difference in the dissolution profiles of the Ti discs treated at 40°C and 60°C. Our findings show

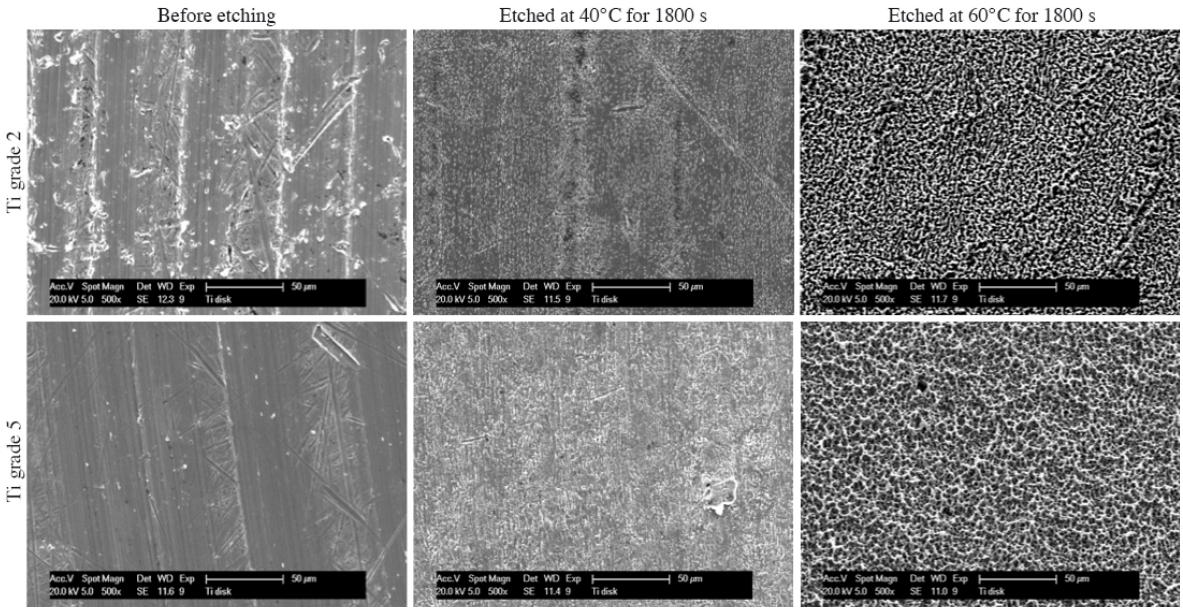

Figure 3. SEM images of grade 2 and grade 5 titanium discs before etching and after etching in HCl at 40°C and 60°C for 1800 seconds.

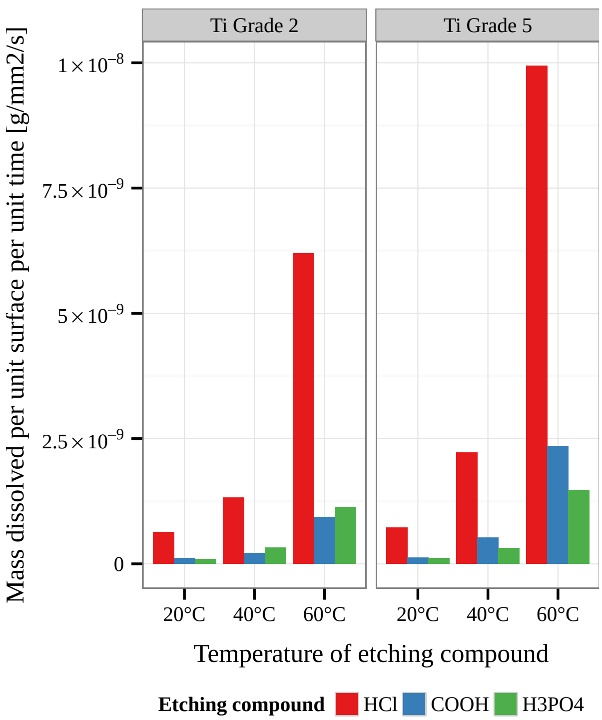

Figure 4. Mass dissolution per unit time of Ti grade 2 and Ti grade 5 in each etching compound.

that increasing the temperature has a more pronounced effect on the mass reduction of Ti grade 2 than the prolonged treatment time (Figure 5).

The same treatment parameters were found to be favorable to create even surfaces on Ti grade 5 discs as on Ti grade 2 discs. The etching of Ti grade 5 in HCl at 40°C for 1800 seconds completely removed the machining marks from the surface of the discs (see Figure 3). Increasing the temperature from 40°C to 60°C resulted in densely pitted surfaces within the same (1800 seconds) treatment period (see Figure 3). Concerning the dissolution profiles of Ti grade 5, increasing the temperature of the 30% HCl etchant resulted in more intense mass reduction of the Ti grade 5 than Ti grade 2 discs (Figure 5).

Interestingly, higher temperatures increased the dissolution rate of both the Ti grade 2 and Ti grade 5 samples irrespective to the composition of the etchant at 60°C. Ti grade 5 showed higher dissolution rates than Ti grade 2 discs and the effect of increased temperature was higher this case than on pure titanium (Figure 4).

The profile roughness measurements did not unambiguously reflect what was observed visually. The roughness of both Ti grade 2 and Ti grade 5 showed slight tendencies to decrease when etched in 30% of HCl at 40°C for 1800 seconds and increase when etched in 30% of HCl at 60°C for the same duration, however neither changes were statistically significant. (Figure 2) The direction of these changes can be explained by the removal of burr in the case of the lower temperature and by the appearance of pits in case of the higher, however we expected a more distinct effect such as those apparent in the optical tests.

5. Conclusion

Our results show that the optical characterization of an etched titanium surface can be more informative concerning biological performance than the mechanical measurement of the surface roughness. The production of an oxide layer with pitted surface texture on a titanium implant in order to support its osseointegration may be achieved at the cost of considerable material loss depending on the chemical composition of the titanium. Ti grade 5 shows higher dissolution rates

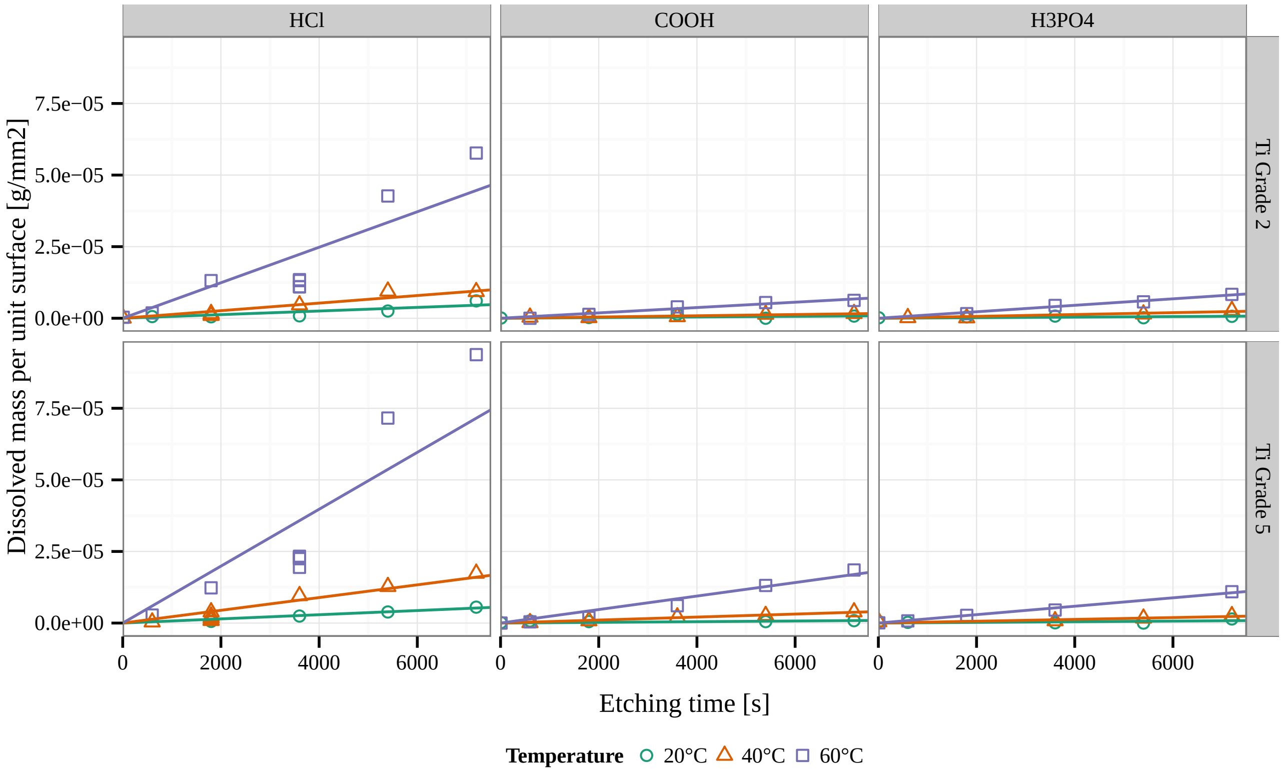

FIGURE 5. Dissolution profiles of Ti grade 2 and Ti grade 5 discs in 85% H_3PO_4, in the compound of 30% $(COOH)_2 \times 2H_2O$ and 30% H_2O_2 and 30% HCl at temperatures of 20°C, 40°C and 60°C.

than Ti grade 2 that might be attributed to the potential difference of its alloying compounds creating an electrochemical cell where the etchant also acts as an electrolyte. From a practical point of view, the uncontrolled etching may adversely affect the fine geometrical structures of dental implants, like the self-tapping part of the thread. Blunted threads may cause undue mechanical stress to the bone tissue during insertion that may detrimentally affect osseointegration. Our team plans to investigate the optimal combination of etching time and temperature in terms of material loss and surface roughness for various etchants and their effect on the fine geometry of dental implant screws.

Acknowledgements

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