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# Surface treatment of titanium dental implant with $H_2O_2$ solution

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**Abstract:** The surface treatment is important for titanium and its alloys as promising candidates for dental implantation due to their bioinert surface. In this analysis, titanium surface samples were modified using $H_2O_2$ solution at different times up to 72 h to boost their bioactivity. According to the results of the field emission scanning electron microscopy test, some nanostructures are formed on the surface of treated titanium samples and increased in size by increasing the time of treatment up to 24 h. After 24 h of application, the sharpness of nanostructures decreased and the micro-cracks and discontinuity in the coating surface increased. The results of the X-ray diffraction study and Raman spectroscopy revealed that anatase ($TiO_2$) was formed on the surface of treated titanium samples. The peak intensity of Raman spectroscopy increased with an improvement in treatment time of up to 24 h and then decreased due to the discontinuity of the coating. Full wettability and ability to form apatite were reached at 6 h of treatment. It is clear that the treatment time has a significant effect on the surface treatment of titanium using the $H_2O_2$ solution.

**Keywords:** titanium implant; surface treatment; hydrogen peroxide; anatase; dental implant

## 1. Introduction

One of the major problems with dental and orthopedic titanium implants is the friction of the interface between the implant and the surrounding hard tissue. Problems arising from lack of fixation include wear and tear of the drug, movement and displacement of the implant, and consequent contamination of the tissue around the implant [1]. The fixation of implants is made possible by three different methods, including mechanical, biological, and biochemical paths. Among all metallic biomaterials, titanium tends to be more suitable for load-bearing implantation due to its low elasticity [2], good corrosion resistance and biocompatibility [3], and fatigue life [4]. Nevertheless, titanium and its alloys are bioinert. Improving their bioactivity is therefore still a problem. Generally speaking, the enhancement of the surface bioactivity of titanium implants can be achieved using two different methods: (i) bioactive coating deposition such as hydroxyapatite (HA) , bioglass (BG), etc. on the surface of

titanium, (ii) bioactive phase formation *in situ* (anatase, rutile, etc.) using processes such as alkali-heat treatment [5], $H_2O_2$ treatment [6], and direct oxidation in air [7].

The latter type of surface treatment is superior to the former in that it offers greater bioactive layer adhesion (without any gap between the coating layer and the substrate) [7]. These methods result in the deposition of titanium oxide (both anatase and rutile phases) on the surface of the titanium.

Both of the anatase and rutile phases are bioactive; rutile is thermodynamically more stable than anatase at ambient temperature, anatase is kinetically more stable than rutile at ambient temperature, and anatase to rutile transformation occurs at high temperatures [8]. While anatase is transformed into rutile at temperatures above 500°C [9], its transformation will be postponed to higher temperatures for a thin film of anatase (up to 900°C) [10].

Wu [6] oxidized the surface of titanium using an $H_2O_2$ solution at 80°C for 72 h to form anatase or rutile on the surface of titanium without any post-heat treatment. According to our recent researches, $H_2O_2$ treatment is a corrosive phenomenon and reduces the mechanical properties of titanium scaffold [11]. We also showed that surface treatment of titanium alloy with $H_2O_2$ solution for 30 min was not effective compared to the alkali treatment [12] and that $H_2O_2$ treatment for 30 min did not significantly boost the bioactivity and cytocompatibility of titanium alloy. Karthega *et al.* [13] reported that surface treatment of titanium with a 15wt% $H_2O_2$ solution is more effective than 5wt% and 25wt% $H_2O_2$ solutions for 1 h. Wen *et al.* [14] used the $H_2O_2$ solution to modify the surface of gradient structured titanium up to 48 h.

According to our recent research [15], the surface of the $H_2O_2$ treated titanium implant prior to heat treatment consists of amorphous titania, while after heat treatment at 600°C for 1 h, it is transformed into crystalline anatase which is a bioactive phase. According to the literature, different times of hydrogen peroxide treatment have been used by researchers to improve titanium surface bioactivity, but the correct period for the application with hydrogen peroxide has not yet been clearly established. In this analysis, titanium surface samples were treated using $H_2O_2$ solution at different times to study the effect of the treatment time on the surface properties of titanium.

## 2. Materials and methods

### 2.1. Surface treatment of titanium

Titanium samples (Grade 2: Kobe steel company, Japan) with a thickness of 1 mm were cut to a depth of 1 cm × 1 cm and their surfaces were polished using 400 grit sandpaper to extract naturally formed oxides. The samples were then washed with 5 min sonication in ethanol and then in water.

Titanium samples were submerged in 15wt% $H_2O_2$ solution at 80°C for 1, 6, 24, 48, and 72 h for the formation of titania gel. After that, the samples were washed with distilled water, dried at 40°C for 24 h, and heat-treated at 600°C for 1 h for crystallization of the gel-like titanium layer [15].

**2.2. Sample characterization**

Field emission scanning electron microscopy (FESEM, JEOL, JSM-7500, Japan) using a secondary electron detector was used to study the surface morphology of treated and untreated titanium samples. X-ray diffraction (XRD, Smart Lab, Rigaku Co., Ltd., Japan) was used to test the phases developed on the surface of the treated and untreated samples. The diffraction pattern was obtained by using Cu-Kα radiation with a wavelength of 0.1540 nm in the range of $20° < 2\theta < 80°$ with a phase scale of 0.05°. The time of each step was 1 s.

Raman spectra were determined using Raman spectroscopy (Jasco, NRS-3200, Japan) in a range of 100–800 $cm^{-1}$ using a green laser beam with a wavelength of 532 nm. The collection was carried out with an exposure time of 600 s, an optical objective lens with a magnification of ×100, and a diaphragm diameter of 100 μm.

The wettability of treated and untreated titanium samples was studied using a static water contact angle test. A 4 μL droplet of distilled water was gently placed on the surface of the samples using the micro-syringe contact angle instrument (Contact angle meter XCA-50), a snapshot of the droplet was taken after 10 s, and the contact angle was measured. The test was repeated three times and the mean values were recorded.

The *in vitro* apatite forming ability was examined by immersion of the treated titanium samples in the simulated body fluid (SBF) at the constant temperature of 37°C without stirring according to the Kokubo protocol [16]. After 7 d of immersion, the samples were collected, carefully rinsed with distilled water, and dried at 40°C for 24 h. The surfaces were eventually analyzed by SEM (scanning electron microscopy) for possible hydroxyapatite formation.

**3. Results and discussion**

**3.1. Microscopic observation**

The surface morphology of titanium samples was studied using FESEM and their micrographs are shown in Fig. 1. This figure shows that some nanostructures are formed on the surface of treated titanium samples and the thickness of the coating seems to have improved with an increase in treatment time. Of course, further micro-cracks and discontinuity can be seen on the surface of the coating after 6 h of application. The surface nanostructures are suitable for cell adhesion and growth [17]. Furthermore, a surface film with a consistent thickness without any discontinuity decreases the direct contact between the metal implanted and the surrounding tissue or body fluids and also limits the possible release of ion *in vivo*. Thus, according to the findings of the

microscopic experiments, the optimal length of treatment tends to be 6 h (a higher number of delicate nanostructures and fewer minor cracks on the surface). Also, while surface morphology and roughness have an effect on cell adhesion and proliferation [18–19], and the untreated sample treated for 1 h does not have significant structures on their surfaces, they do not appear to be suitable for cell proliferation.

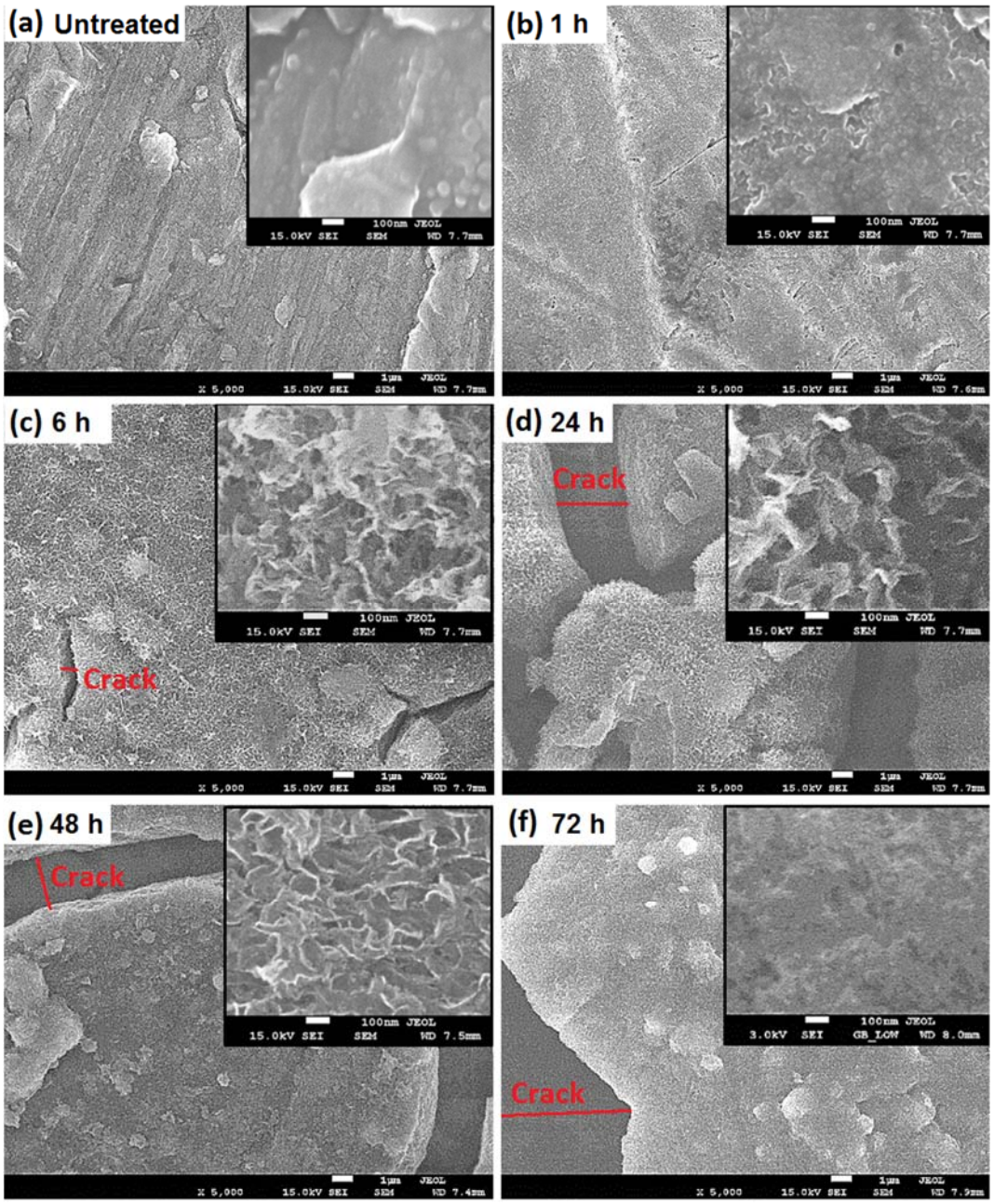


**Fig. 1. FESEM micrographs of the untreated and treated titanium samples at different treatment times: (a) untreated; (b) 1 h; (c) 6 h; (d) 24 h; (e) 48 h; (f) 72 h.**

FESEM micrograph of the treated titanium sample for a prolonged period of time (Figs. (1)e and 1(f) for 48 or 72 h) shows that some coating layer has been removed from the surface and a heterogeneous coating has been

formed on the surface of the titanium. This could be attributed to the premature thickening of the surface by the passage of time and also corrosive nature of $H_2O_2$ [11]. It seems that as time passes, the thickness of the titanium oxide layer on the surface of titanium and its detachment will increase.

### 3.2. Phase analysis using XRD

In order to study the phases on the surface of treated titanium, the X-ray diffractometry was used and the patterns are shown in Fig. 2. The X-ray diffraction patterns suggest that the surface of treated titanium samples consists of titanium (PDF No. 00-005-0682) and anatase (PDF No. 00-001-0562). Of course, no anatase phase can be observed on the surface of treated titanium for 1 h. Anatase is a bioactive phase that can improve the apatite forming ability and also osseointegration of titanium implant [20]. In fact, X-ray diffraction patterns suggest that no corrosion or extra phase has been formed on the surface of the treated titanium samples.

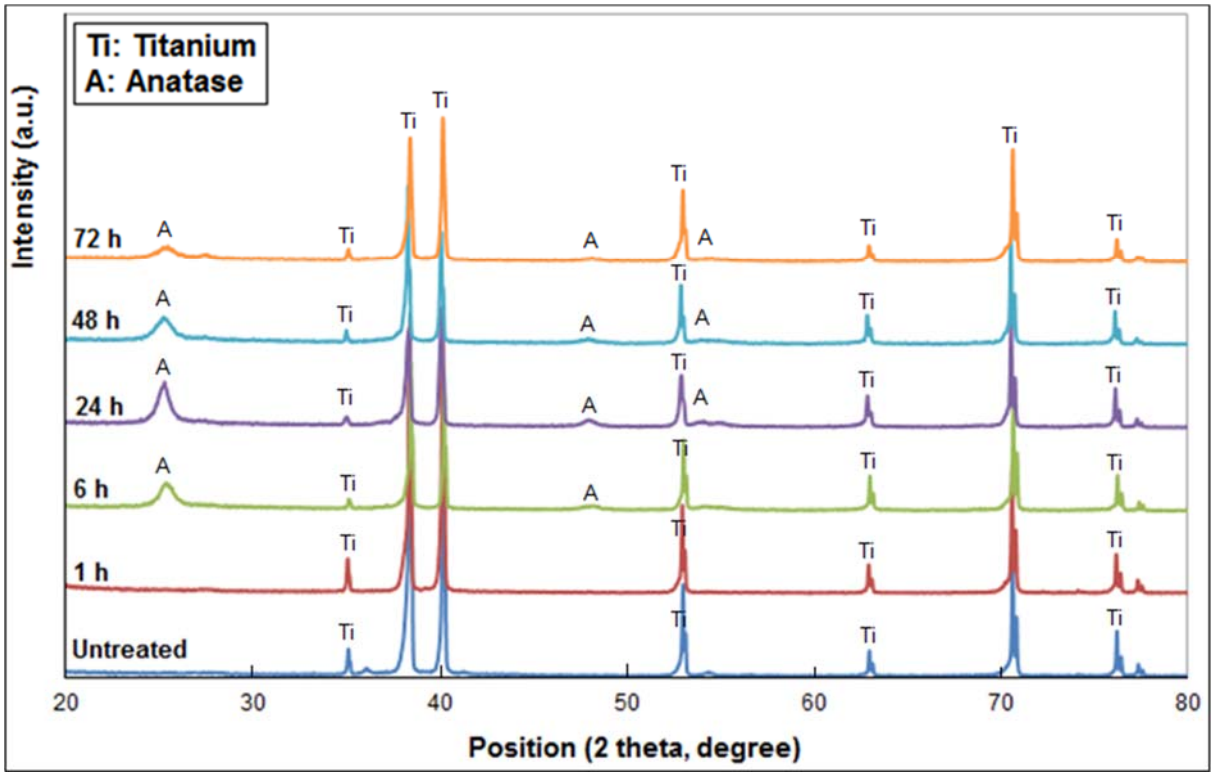


**Fig. 2. X-ray diffraction patterns of the untreated and treated titanium samples at different times.**

### 3.3. Phase analysis using Raman spectroscopy

Fig. 3 shows the Raman spectras of untreated and treated titanium samples at different times. According to this figure, the surface of all treated samples consists of only anatase (Raman shift of 143, 195, 396, 518, and 639 $cm^{-1}$) and no other phase is detectable, which confirms the results of X-ray diffraction analysis. Additionally, the results of the Raman spectroscopy indicate that the intensity of Raman spectra increased by increasing the time of treatment up to 24 h and then decreased. This suggests that, over time, a finer layer of anatase was formed on

the surface of titanium, but with an increase in treatment time of more than 24 h, a greater number of microcracks were formed and some parts of anatase coating were detached from the surface, resulting in lower peak intensity. This report is in good agreement with the observation of the FESEM study.

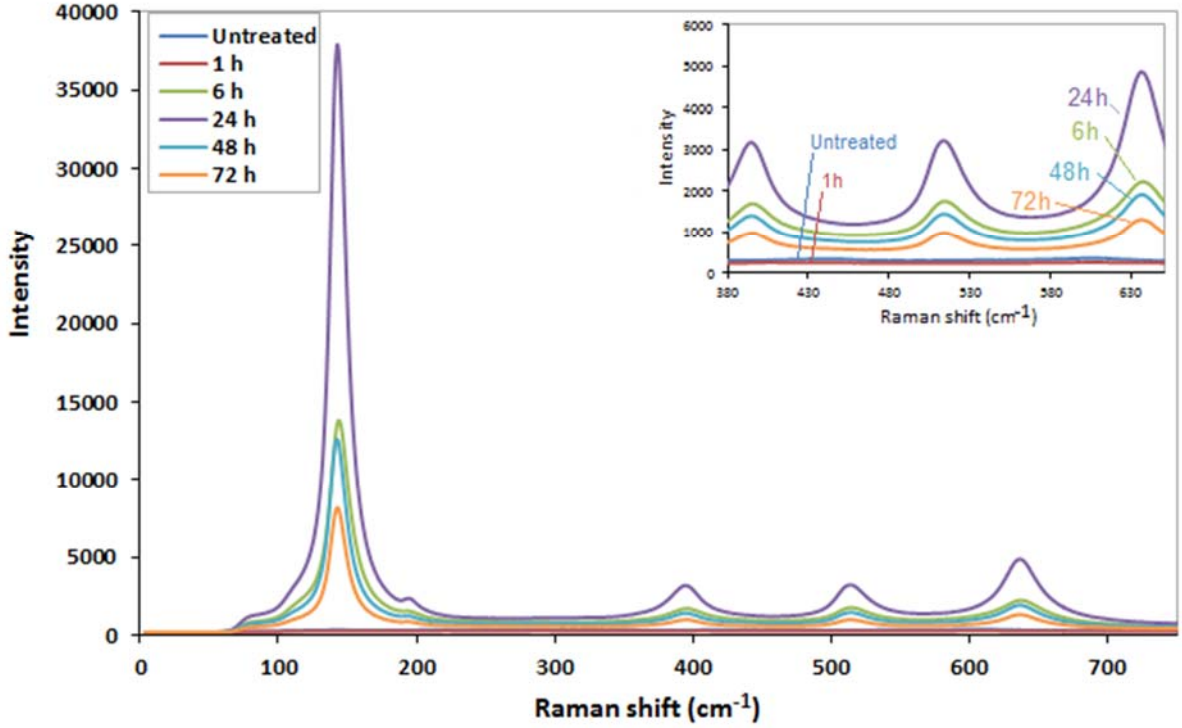


**Fig. 3. Raman spectras of the untreated and treated titanium samples at different times.**

### 3.4. Wettability of treated titanium samples

The results of the wettability measurement of titanium samples shown in Fig. 4 show that the touch angles of the untreated titanium and the treated titanium samples for 1, 6, 24, 48, and 72 h are 63°, 69°, 32°, 57°, 54°, and 50°, respectively. It is clear that the minimum angle of contact with water or maximum hydrophilicity is related to the titanium sample surface treated for 6 h. In addition, different surface morphologies and coating thicknesses have contributed to different water contact angles of the treated titanium samples.

A smaller angle of contact with water leads to better wettability or more hydrophilicity, which results in better apatite forming ability and also *in vivo* protein and cell adhesion [21–22], as well as faster osseointegration [23]. It is clear that the 24 h contact angle of the treated titanium improved more than the 6 h contact angle of the study. This is because of crack and discontinuity formation on the titania coating. After 24 h of treatment, the contact angle decreased again due to the newly formed titania on the bare areas (cracks).

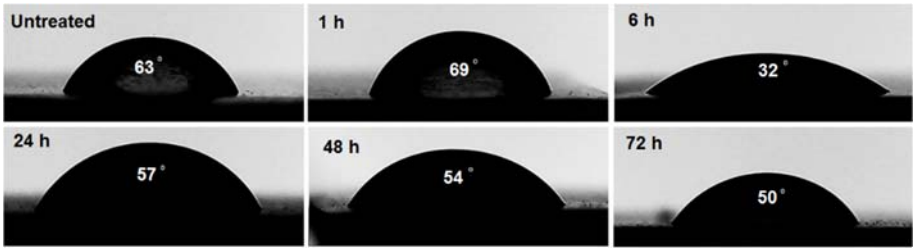


**Fig. 4. Water contact angles of the untreated and treated titanium samples at different times.**

In addition, the water contact angle is affected by surface chemical composition, morphology, and surface energy [24]. All of the parameters listed have an effect on cell adhesion and osseointegration of the implant. The smaller water contact angle of the implant facilitates cell adhesion and could reduce the bone healing time.

### 3.5. Apatite forming ability of the treated titanium samples

The results of SEM examination of the untreated and treated titanium samples after 7 d of immersion in SBF show that the number and size of bone-like apatite particles deposited increased with increased length of exposure. More apatite forming ability expresses better osseointegration *in vivo*, which can lead to faster implant/surrounding tissue fixation and shortened healing time. According to Fig. 5(b), the hydroxyapatite (HA) particles tend towards nucleation and development of the surface grooves.

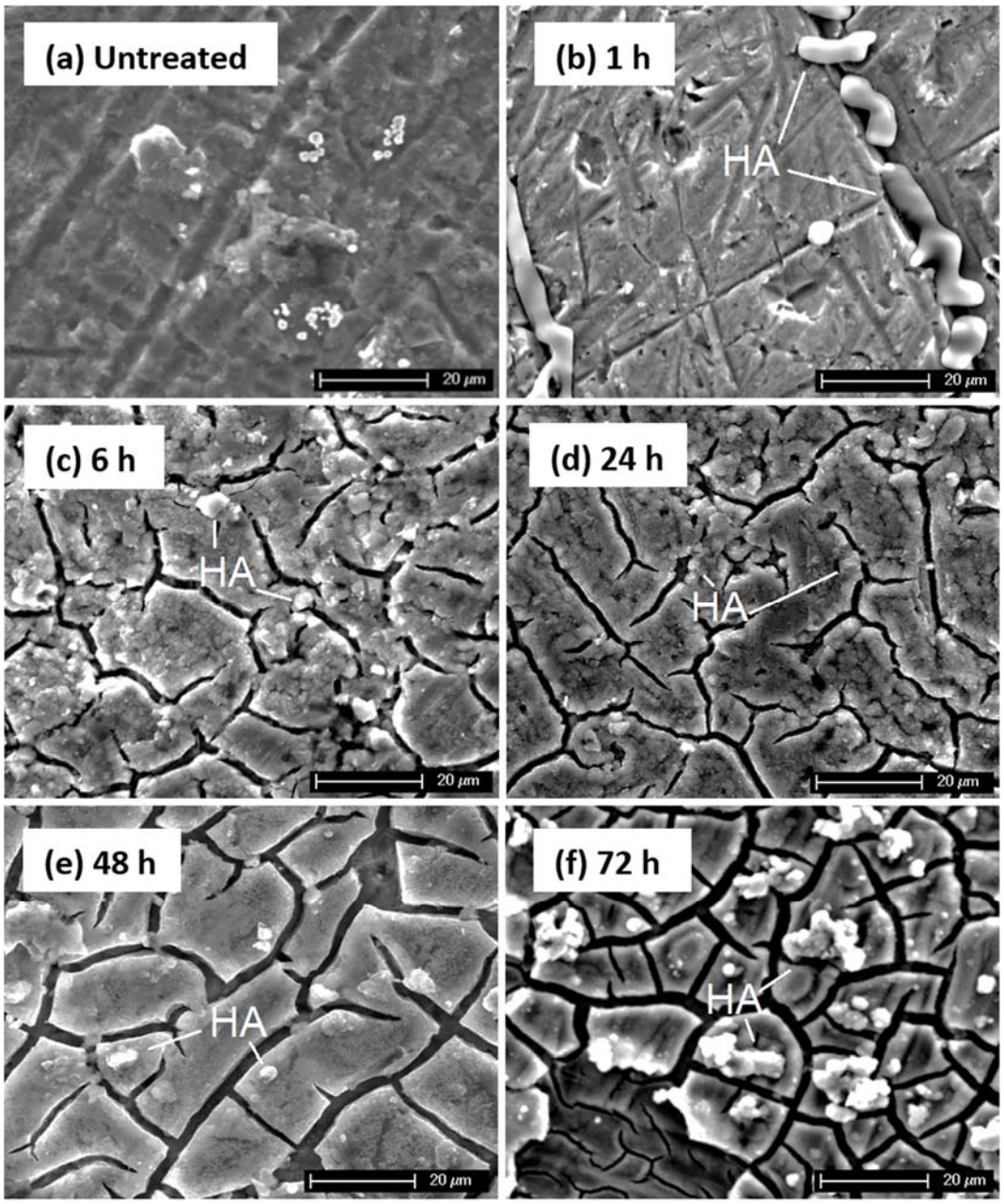


**Fig. 5. Bone-like apatite formation on the surface of untreated and treated titanium samples at different times (after 7 d of immersion in SBF): (a) untreated; (b) 1 h; (c) 6 h; (d) 24 h; (e) 48 h; (f) 72 h.**

Although Osaka *et al.* [25] have reported that apatite forming ability of titanium improved with $H_2O_2$ treatment and that the concentration of $H_2O_2$ and its pH value have an influence on process efficiency, it can be seen that the time of treatment also has a significant impact on process output. Typically, according to the results of FESEM observations, the $H_2O_2$ treatment of titanium samples for 6 h led to the formation of nanostructure on the surface of titanium, including minor crack and discontinuity. In addition, the results of XRD analysis and Raman spectroscopy show that anatase was formed on the surface of treated titanium for 6 h with almost high intensity (thickness), and the minimum contact angle with water was obtained. Therefore, the optimum time for the treatment of titanium using the $H_2O_2$ solution seems to be about 6 h and the longer periods lead to the removal

and cracking of the titanium coating. The $H_2O_2$ treatment involves three steps of titanium oxidation, titania gel formation, and titanium dissolution [25]. At the start of the treatment, titanium is oxidized and titania gel is formed, but with an improvement in the treatment period, more titanium is dissolved in $H_2O_2$ solution [14] and more discontinuity and cracks are formed on the surface, and more sections of the coating become removed from the surface. As reported by other researchers, treatment with $H_2O_2$ leads to anatase and also the formation of the Ti–OH functional group on the surface of titanium [13], so that selection of appropriate treatment time will transform it into a successful method for surface treatment of titanium implants.

**4. Conclusions**

The surface of the titanium sample as a dental implant was modified using the $H_2O_2$ solution at different treatment times at 80°C. The results show that the thickness of anatase nanostructures on the surface of titanium increased by increasing the time of treatment, which improves wettability and the ability of apatite to bind titanium up to 24 h. But the discontinuity and micro-cracks of the surface have also increased. It is concluded that the duration of treatment significantly affects surface morphology, wettability, and ability to form apatite. Choosing an appropriate time of treatment to make a crack-free bioactive phase could make titanium a more attractive choice for dental implantation. The results show that the optimum time for surface treatment of titanium with $H_2O_2$ solution at 80°C is approximately 6 h.

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