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Effect of water aging on the apatite formation of a low-modulus Ti–7.5Mo alloy treated with aqueous NaOH

Hsueh-Chuan Hsu · Hsi-Kai Tsou · Shih-Kuang Hsu · Shih-Ching Wu · Chien-Hung Lai · Wen-Fu Ho

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Abstract The objective of this experiment was to develop biomimetic calcium phosphate coatings on low-modulus Ti–7.5Mo substrates treated with NaOH aqueous solutions and subsequent water aging before soaking them in simulated body fluid (SBF). Specimens of commercially pure titanium (c.p. Ti) and Ti–7.5Mo were initially treated with 5 M NaOH at 60 °C for 24 h, resulting in the formation of a porous network structure composed of sodium titanate ($Na_2Ti_5O_{11}$). Afterward, the specimens were aged in distilled water at 80 °C for 12, 24, or 48 h, and subsequently immersed in 1.5SBF at 37 °C for either 1 or 13 days. The calcium phosphate-forming abilities of the c.p. Ti and Ti–7.5Mo achieved by a single NaOH treatment were low, but were significantly increased by the water aging. The amount of calcium phosphate deposited on the Ti–7.5Mo after NaOH treatment and subsequent water aging for 12 or 24 h was much greater than other conditions. The calcium phosphate-coated Ti–7.5Mo has strong potential as an artificial bone substitute or in other hard tissue-replacement materials with heavy load-bearing requirements due to a favorable combination of bioactivity, low elastic modulus, and low processing costs.

H.-C. Hsu · S.-K. Hsu · S.-C. Wu
Department of Dental Laboratory Technology, Central Taiwan University of Science and Technology, Taichung, Taiwan, ROC

H.-C. Hsu · S.-K. Hsu · S.-C. Wu
Institute of Biomedical Engineering and Material Science, Central Taiwan University of Science and Technology, Taichung, Taiwan, ROC

H.-K. Tsou
Department of Neurosurgery, Taichung Veterans General Hospital, Taichung, Taiwan, ROC

C.-H. Lai
Department of Mechanical and Automation Engineering, Da-Yeh University, Changhua, Taiwan, ROC

W.-F. Ho (✉)
Department of Materials Science and Engineering, Da-Yeh University, No. 168, University Road, Dacun, Changhua 51591, Taiwan, ROC
e-mail: fujii@mail.dyu.edu.tw

Introduction

Titanium and its alloys are favored as orthopedic implants due to their biocompatibility, excellent corrosion resistance, good mechanical properties, and lightness [1]. It is well documented that titanium and its alloys become encapsulated by fibrous tissue after implantation into defective bones [2, 3], with the result that these metals cannot bond directly to surrounding bones [4, 5]. Various surface modifications have been attempted to improve the bone conductivity of these metals, such as plasma-spraying, sputter-deposition, sol–gel coating, electrophoretic deposition, or biomimetic deposition [6–13]. Of these, the most popular process is plasma-spraying of ceramics on the titanium substrate. One of the most widely accepted and commercialized bioactive coating materials is plasma-sprayed hydroxyapatite (HA) [12, 13]. Although many favorable clinical results have been reported, there have been several problems with its porosity, low fatigue strength, degradation, and delamination during long-term implantation [14–17]. Recently, investigation for HA has also been greatly focused in biomaterial research since its chemical and crystallographic properties are similar to the inorganic component found in natural bone [18]. In addition, HA ceramics possessing 10-μm-order micropatterned surfaces are promising materials for cell engineering.

Suetsugu et al. [19] utilized a periodical precipitation in a gel sheet to create two-dimensional regular stripe patterns of HA with 10-µm-order pitch anticipating an application to cell culture substrates.

Several researchers have reported that certain chemical treatments can be implemented to modify titanium in order to achieve further chemical bonding of the implant with bone [20–24]. Ni et al. [25] used decyl bis phosphonate (DBP) and collagen I to modify Ti–6Al–4V through layer-by-layer technique to improve its bioactivity. As is well known, when titanium is treated with an NaOH aqueous solution, a thin sodium titanate layer is formed on its surface, and a bone-like apatite layer can be formed after it is soaked in a simulated body fluid (SBF) [21, 22]. Biomimetic deposition of HA has also attracted widespread interest because of its low deposition temperature and good step coverage [26]. Moreover, several researchers have achieved greater bone-to-implant contact for biomimetic calcium phosphate coatings than for uncoated titanium implants [6, 27]. Besides, Boyd et al. [28] sought to validate the amorphous nature and composition of the apatite surface layers observed on Zn-GPCs after immersion in SBF using transmission electron microscopy. The apatite layer is similar to that believed to occur in the natural mineralization process in bone and indicates that these materials will likely bond directly to living bone tissue.

Titanium and titanium-based alloys which have been widely used in the field of biomaterials are commercially pure titanium (c.p. Ti), Ti–6A1–4V ELI, and Ti–6A1–7Nb. The Ti–6A1–4V alloy, which was originally developed as an aerospace material, has become one of the most popular applications due to its corrosion and fatigue resistance, in addition to its exceptional strength in comparison to c.p. Ti [29]. However, recent studies have reported that aluminum in Ti–6A1–4V can be released into the human body from the alloy and lead to mental disease [30]. Another component of Ti–6A1–4V that can be released into the human body is vanadium, which may accumulate in tissues or cells and damage cells due to its strong cytotoxicity [31]. These concerns have led to the development of Al- and V-free titanium alloys with mechanical and corrosion properties similar to those of Ti–6Al–4V.

Another important requirement for implants which are designed to replace or interact with bone is low elastic modulus, matching as closely as possible that of the surrounding bone tissue [32]. Ti–7.5Mo is a new α''-phase alloy possessing a lower elastic modulus, an improved strength/modulus combination [33], and excellent corrosion resistance [34]. However, as with other biomedical titanium alloys, it remains as a bioinert material.

Classical biomimetic calcium phosphate coatings normally require an immersion period of about 14–28 days with replenishment from an SBF solution. Recently, efforts have been made to accelerate this process to increase its practical utility [35–38]. In our previous study [39], bioactive coatings on c.p. Ti and Ti–7.5Mo were prepared by immersion in a NaOH solution. In that study, the apatite-forming ability of alkali-treated Ti–7.5Mo was found to be greater than that of alkali-treated c.p. Ti when immersed in 5, 10, or 15 M NaOH aqueous solutions. Also, HA coatings were formed on the surfaces of c.p. Ti and Ti–7.5Mo which were acid-etched and subsequently alkali-treated before samples were soaked in SBF. The c.p. Ti and Ti–7.5Mo subjected to both acid etching and alkaline treatment showed a greater level of apatite-forming ability than that of c.p. Ti and Ti–7.5Mo subjected to only NaOH treatments [40]. In this study, attempts were made to develop a biomimetic calcium phosphate coating on low-modulus Ti–7.5Mo alloy substrates treated with NaOH aqueous solutions and water aging before immersion in SBF. The results were compared with c.p. Ti, which was chosen as a control. Moreover, high-heat treatments were avoided because the metastable α''-phase Ti–7.5Mo alloy is very sensitive to temperature changes. Furthermore, a high-temperature treatment process tends to result in the crystallization of the hydrogel layer, thereby reducing the ionic activity and decreasing the rate of apatite nucleation and formation [41, 42]. Finally, the effect of varying water aging time on the apatite-forming ability in an SBF of c.p. Ti and Ti–7.5Mo subjected to NaOH–water treatment was also evaluated.

Experimental procedures

The materials used for this study included c.p. Ti and a Ti–7.5Mo alloy. (Note: All compositions are expressed by mass.) All the materials were prepared from raw titanium (99.8% pure) and molybdenum (99.95% pure) by using a commercial arc-melting vacuum-pressure-type casting system (Castmatic, Iwatani Corp., Japan). The ingots, of approximately 20 g, were remelted three times, for about 55 s each to improve their chemical homogeneity. Prior to casting, the ingots were again remelted. The difference in pressure between the two chambers allowed the molten alloys to instantly drop into a graphite mold at room temperature.

In this study, the cast alloys were sectioned by using a Buehler Isomet low-speed diamond saw to obtain specimens. Flat sheets of c.p. Ti and of Ti–7.5Mo, $1 \times 10 \times 10\ \mathrm{mm}^3$ each, were used as substrate materials. The surfaces of the metals were abraded to the final level of 2000-grit paper. The metal substrates were then ultrasonically cleaned in distilled water, acetone, and ethanol for 20 min, respectively, after which the substrate plates were again cleaned in distilled water for another 10 min.

Subsequently, the cleaned specimens were immersed in 5 M NaOH aqueous solutions at 60 °C for 24 h. The temperature was maintained by using a water bath. After the 24-h incubation period, the substrates were gently washed with distilled water and dried at 40 °C for 24 h.

After this NaOH treatment, the substrates of c.p. Ti and of Ti–7.5Mo were gently washed with distilled water, and then immersed in 20 mL of distilled water at 80 °C for either 12, 24, or 48 h. To save space, 'N' will stand for 'NaOH treatment' and 'W' will stand for 'water treatment'. Moreover, N–W12, N–W24, and N–W48 represent the c.p. Ti or Ti–7.5Mo sample subjected to NaOH treatment and followed by water treatment for 12, 24, and 48 h, respectively. After the respective periods of immersion, the specimens were removed and immediately soaked in 20 mL 1.5SBF to test the capability of c.p. Ti and Ti–7.5Mo to spontaneously form a bone-like apatite layer in vitro. To accelerate the formation of an apatite layer on the treated surfaces, a solution with 1.5 times the strength of standard SBF (1.5SBF) was used in the biomimetic apatite deposition process. The SBF was prepared by dissolving reagent grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 in distilled water. The ionic concentrations of the SBF (vs. human plasma) are listed in Table 1 [43]. Half the treated substrates were immersed in the SBF at 37 °C for 1 day, and the rest for 13 days. The temperature was maintained by using a water bath. After being soaked for selected durations, the specimens were removed from the fluid, washed with distilled water, and air-dried.

After the NaOH treatment and water aging, the surfaces of the c.p. Ti and Ti–7.5Mo specimens were examined by field-emission scanning electron microscopy (FE-SEM; JSM-6700F, JEOL, Japan) and X-ray diffractometry (XRD; MXP-III, Brukers, Germany). Furthermore, changes in the surfaces of the c.p. Ti and Ti–7.5Mo after being soaked in SBF were determined by SEM (S-3000N, Hitachi, Japan), and surface chemical analysis was implemented by energy-dispersive X-ray spectroscopy (EDS) in the SEM. To evaluate the ability and rate of apatite formation on the sample surface, changes in the pH values of the SBF were determined each day by using an electrolyte-type pH meter (Ion 6 meter, Oakton, USA). The weight of the apatite coating on each specimen with a different soaking time was obtained in an electronic balance (SD-200L, Mirage, Japan) with accuracy of ±0.0001 g. The SBF was refreshed after each measurement. Contact angle measurements were implemented to evaluate the wettability of the c.p. Ti and Ti–7.5Mo specimens subjected to various kinds of pre-treatment, measured with Millipore water on an OCA 15 (DataPhysics Instruments, Filderstadt, Germany) with SCA20 software (Dataphysics, Germany).

Table 1 Ionic concentrations (mM) of simulated body fluid compared to human blood plasma [43]

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HPO_4^{2-}	SO_4^{2-}	HCO_3^-
Blood plasma	142.0	5.0	1.5	2.5	103.0	1.0	0.5	27.0
SBF	142.0	5.0	1.5	2.5	147.8	1.0	0.5	4.2
1.5SBF	213.0	7.5	2.3	3.8	221.7	1.5	0.75	6.3

Results and discussion

Surface morphologies after NaOH treatment and water aging

Figure 1 shows the changes in the surfaces of the NaOH-treated c.p. Ti and Ti–7.5Mo substrates after undergoing water aging at 80 °C for 12, 24, or 48 h. After the NaOH treatments, the surfaces of both the c.p. Ti and Ti–7.5Mo substrates exhibited porous network structures. These structures were relatively unchanged after various periods of water aging, but gradually became denser after immersion in water at 80 °C for 48 h. Morphologies of cross-sections of the NaOH-treated and water-aged c.p. Ti and Ti–7.5Mo samples are shown in Fig. 2, where a homogeneous and even reaction layer about 3–6 μm thick can be seen on the substrates. Notably, the thickness of the reaction layer decreased with increasing water aging periods. It is also noteworthy that the Ti–7.5Mo had a thicker reaction layer than the c.p. Ti under the same conditions. Since the sodium titanate hydrogel does not dissolute in water, only ion-exchange between Na^+ ion of the sodium titanate hydrogel and H_3O^+ ions of water can occur in water. As a consequence, it may be difficult to directly correlate the decreasing thickness of the surface layer with ion-exchange mechanism alone. Uchida et al. [44] observed that the porous network structure, which was formed by the NaOH treatment, was apparently unchanged after immersion in water at 40 °C for 48 h, but gradually densified after immersion in water at 80 °C for 24 and 48 h. Although the densification could partially contribute to the diminished thickness of the surface layer after water aging in this study, the precise reasons are not yet completely clear at the moment.

Previous studies have reported that this porous layer is sodium titanate ($Na_2Ti_5O_{11}$) formed after NaOH treatments [39, 45, 46]. Although the XRD patterns of pre-treated c.p. Ti and Ti–7.5Mo are not shown in this study, the results of c.p. Ti and Ti–7.5Mo treated by 5 M NaOH were presented in our previous report [39]. A sodium titanate ($Na_2Ti_5O_{11}$) peak appeared between 29° and 30° in 2θ on all XRD patterns after NaOH treatment of the pre-treated c.p. Ti and

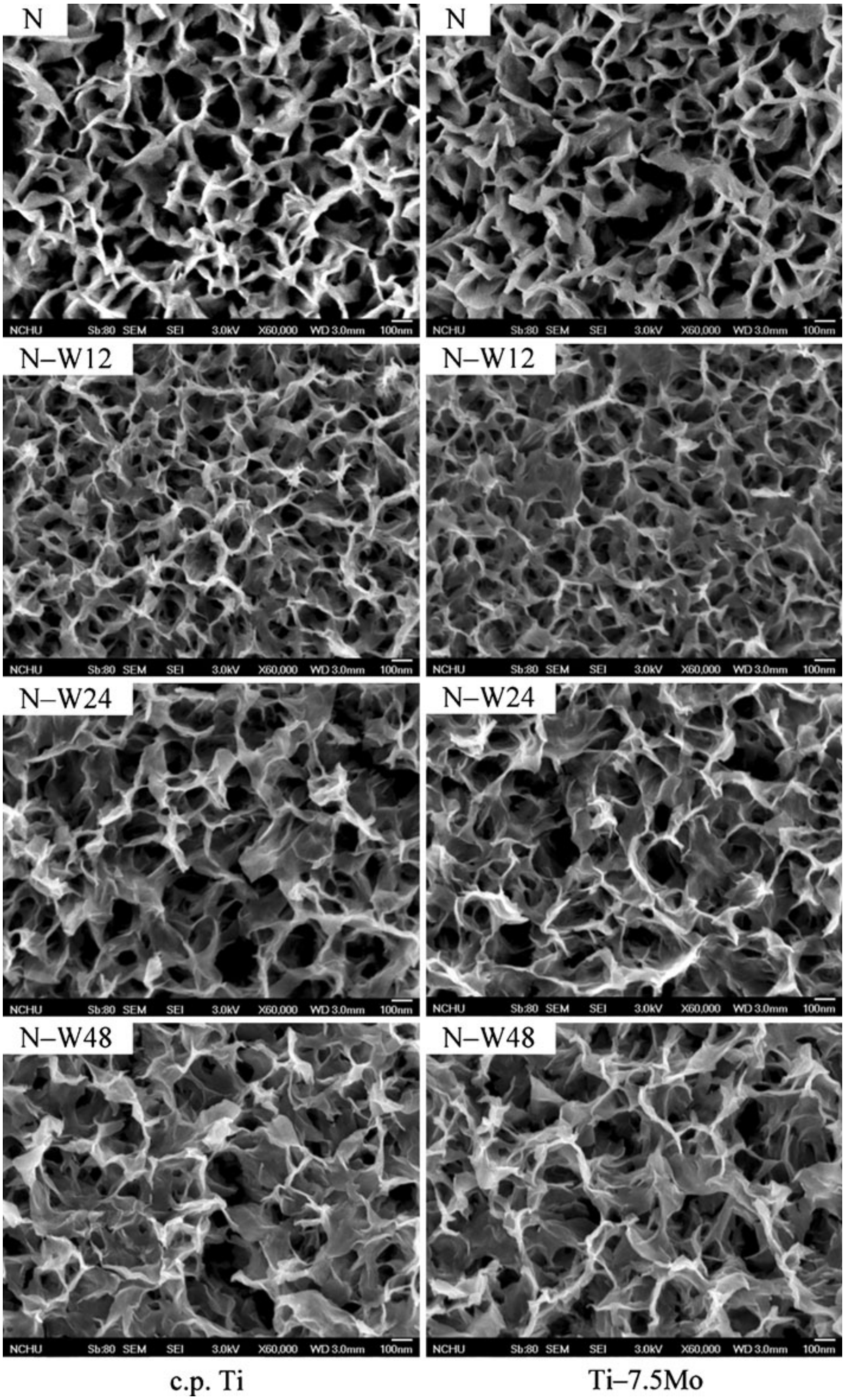


Fig. 1 FE-SEM photographs of surfaces of c.p. Ti (*left side*) and Ti–7.5Mo (*right side*) subjected to NaOH (N) or NaOH–water (N–W) treatments for 12, 24, or 48 h

Ti–7.5Mo samples. When the specimens were aged in distilled water, the sodium ions in the sodium titanate hydrogel were released, which is similar to the process that takes place in SBF [26, 44]. Pattanayak et al. [47] concluded that 5.5 at.% of Na was incorporated into the surface of the c.p. Ti by the 5 M NaOH treatment, then completely removed by subsequent water or HCl treatments. Their finding is in good agreement with the results of EDS in this study, as shown in Fig. 3. The EDS analysis of this reaction layer indicated the presence of Na, Ti, and O-atoms for NaOH-treated c.p. Ti and Na, Ti, Mo, and O-atoms for NaOH-treated Ti–7.5Mo. After subsequent

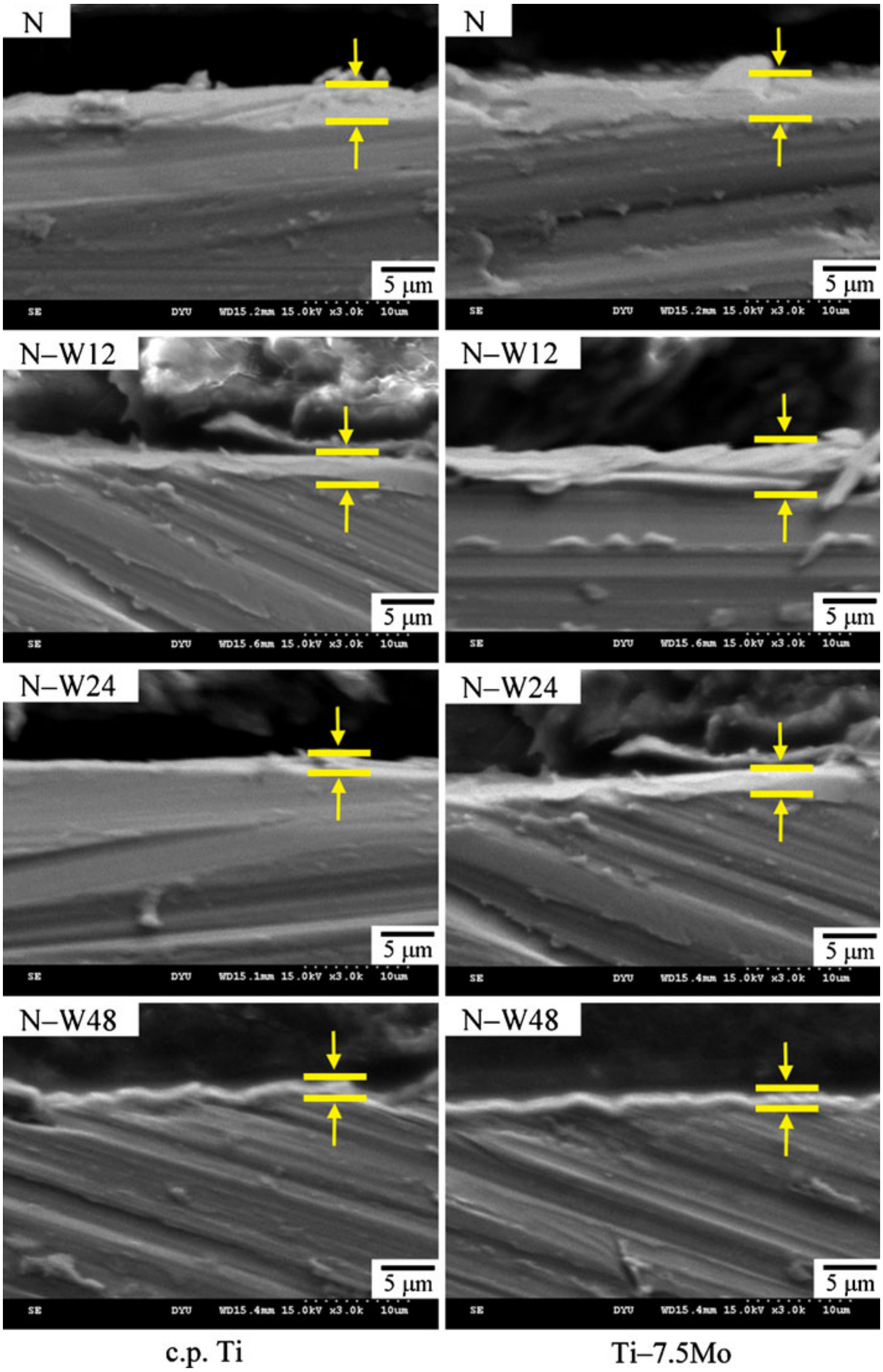


Fig. 2 SEM photographs of cross-sections of c.p. Ti (*left side*) and Ti–7.5Mo (*right side*) subjected to NaOH (N) or NaOH–water (N–W) treatments for 12, 24, or 48 h

water treatment, Na was not detected for 48-h aged Ti–7.5Mo (N–W48). Moreover, there was no detectable Na signal in EDS from the c.p. Ti water-aged for 24 or 48 h (N–W24 or N–W48). Kawai et al. [48] recently proposed that the NaOH- and heat-treated Ti metal gives high and stable apatite-forming ability when the Ti metal was treated with water after the NaOH treatment to partially remove sodium ions in the surface layer, and subjected to heat treatment.

Wettability

In this study, NaOH treatment and water aging were employed to augment the hydrophilicity which generally characterizes enhanced bioactivity [33]. Figure 4 shows the average water-contact angles of the untreated c.p. Ti and Ti–7.5Mo specimens as well as those treated with NaOH and subsequent water aging for 12, 24, or 48 h. Whereas distilled water contacted the untreated samples at angles of

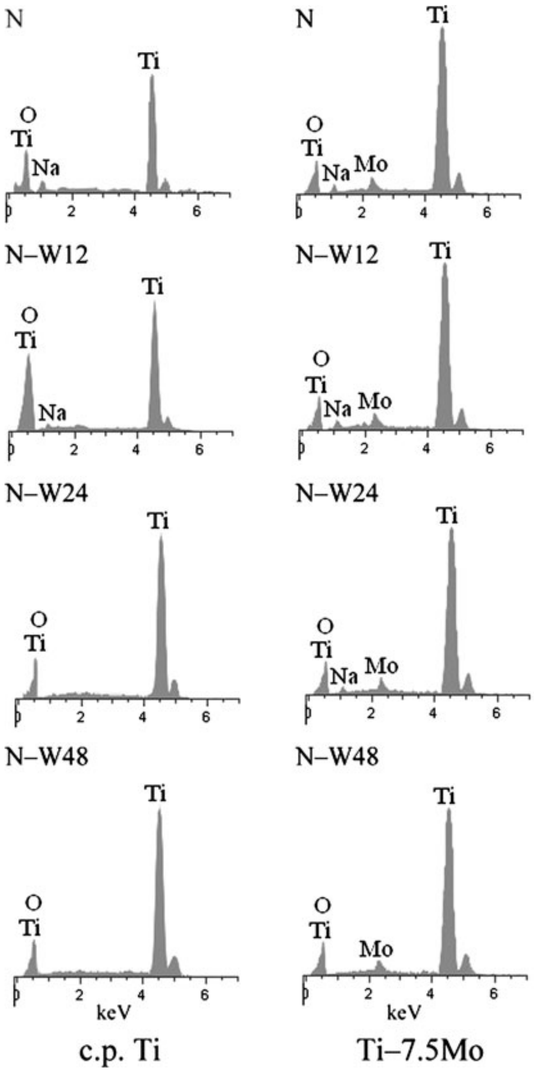


Fig. 3 EDS of surfaces of c.p. Ti (*left side*) and Ti–7.5Mo (*right side*) subjected to NaOH (N) or NaOH–water (N–W) treatments for 12, 24, or 48 h

approximately 26° for c.p. Ti and 28° for Ti–7.5Mo, after subsequent NaOH treatments, the surface became much more easily wetted, thus resulting in a very low contact angle. Moreover, the water-contact angles of the surfaces were further reduced by aging in water. In fact, the contact angles of the samples which were water-aged for 24 h were the lowest, being less than 9° for c.p. Ti and 6° for Ti–7.5Mo. It is also noteworthy that the contact angles of Ti–7.5Mo were significantly lower ($p < 0.05$) than those of c.p. Ti under this condition. Rupp et al. [49] also found that hydrophobic sandblasted/acid-etched c.p. Ti surfaces could be induced into hydrophilic modification by storage in water or an NaCl solution. Therefore, we conclude that the NaOH treatment and water aging greatly influenced the wettability of the c.p. Ti and Ti–7.5Mo surfaces.

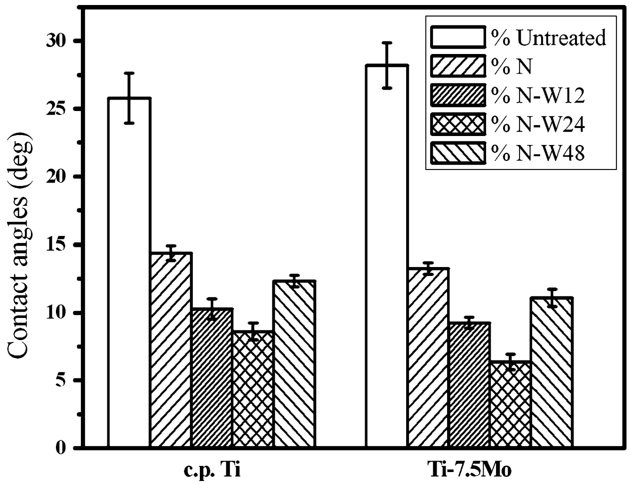


Fig. 4 Average water-contact angles of c.p. Ti and Ti–7.5Mo untreatment (UN), subjected to NaOH (N) or NaOH–water (N–W) treatments for 12, 24, or 48 h

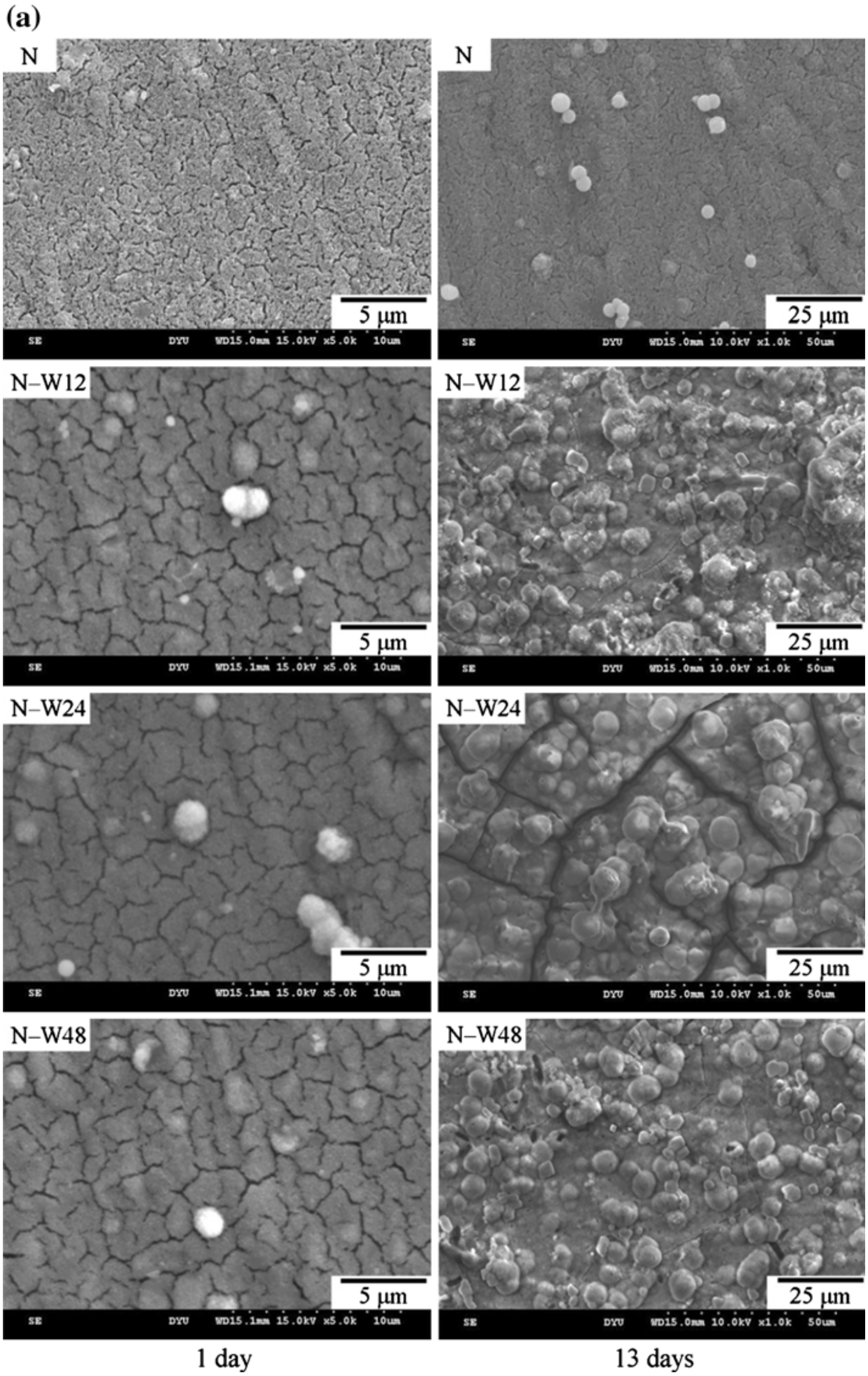
Surface wettability is one of the most important parameters affecting the biological response to an implanted material. This attribute affects protein adsorption, platelet adhesion/activation, and blood coagulation as well as cell and bacterial adhesion [50–53]. Highly hydrophilic surfaces seem more desirable than hydrophobic ones in view of their interactions with biological fluids, cells, and tissues [54, 55]. Furthermore, in a recent animal study, Buser et al. [55] found that a hydrophilic sandblasted/acid-etched surface promoted enhanced bone apposition during the early stages of bone regeneration.

Ca–P precipitation on treated surfaces

Figure 5 shows the SEM photographs of the surfaces of c.p. Ti and Ti–7.5Mo that had been soaked in 1.5SBF for either 1 or 13 days after NaOH treatment and subsequently undergone different periods of aging in water. As can be seen, there was no new particle formation by nucleation on the surfaces which had undergone NaOH treatment and subsequent soaking in 1.5SBF solution for 1 day. However, there were numerous nucleation spheres and deposition on the surfaces of the substrates which had received water aging. Notably, many more isolated or aggregated spheroids having a diameter of approximately 1–2 µm were deposited on the surface of the Ti–7.5Mo than on the c.p. Ti under this condition.

After soaking in a 1.5SBF solution for 13 days, a dense calcium phosphate layer covered the surfaces of the water-aged c.p. Ti and Ti–7.5Mo substrates, depleting the Ca^{2+} and PO_4^{3-} from the surrounding solutions. In contrast, only a few tiny particles, having a diameter of less than 1 µm, were sparsely deposited on the surfaces of the c.p. Ti and Ti–7.5Mo which were not aged in water. This indicates that

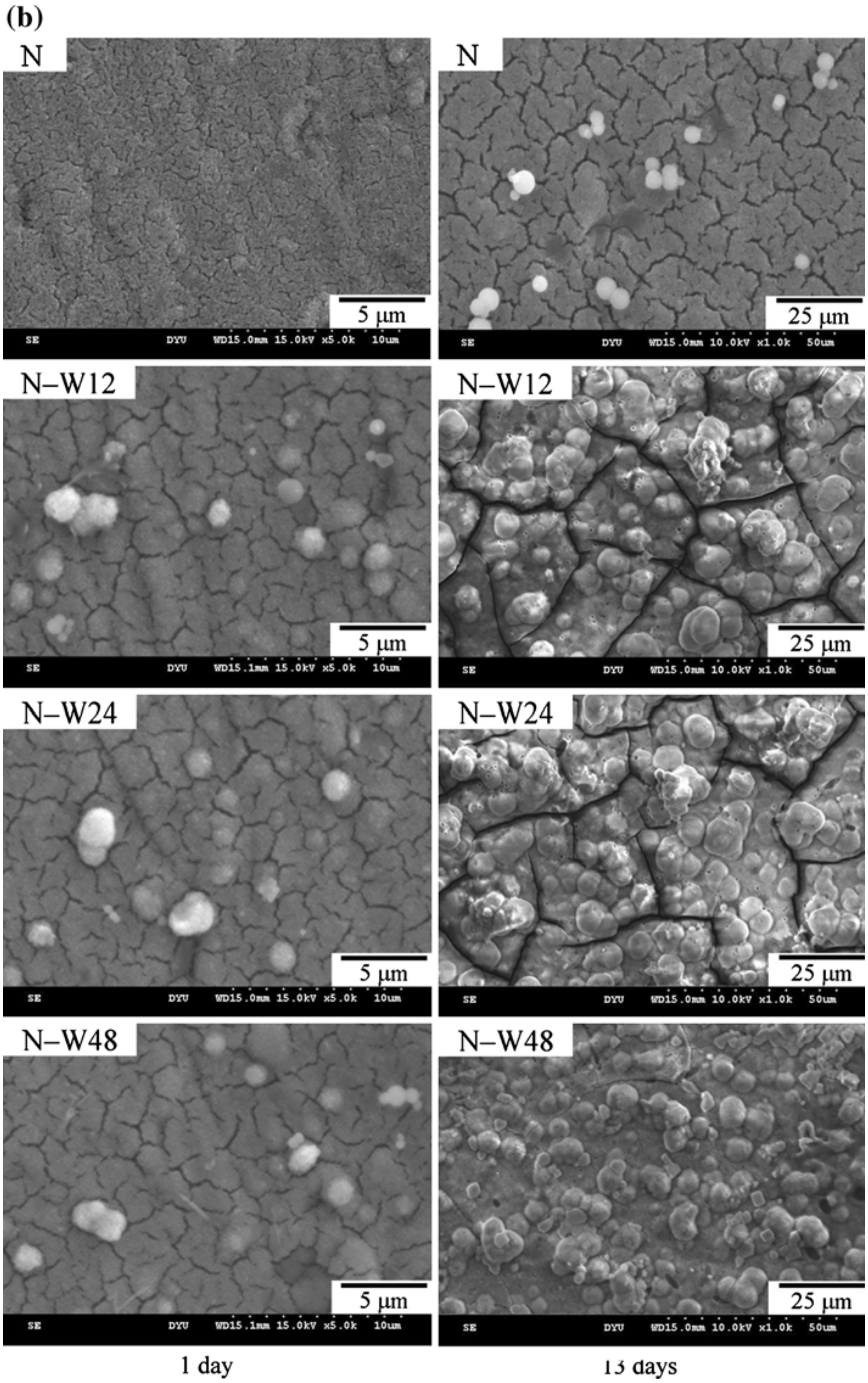
Fig. 5 SEM micrographs of surface morphology of NaOH-treated and subsequently water-aged **a** c.p. Ti and **b** Ti–7.5Mo after soaking in SBF for 1 and 13 days



calcium phosphate can be quickly nucleated and deposited on the surfaces of c.p. Ti and Ti–7.5Mo substrates after NaOH treatment and subsequent water aging. Furthermore, higher calcium phosphate-forming ability can be acquired by subsequent water aging for specific durations, in particular, 12 or 24 h for Ti–7.5Mo and 24 h for c.p. Ti, as illustrated in Fig. 5.

The reasons why the NaOH-treated and water-aged titanium metals show a high calcium phosphate-forming ability can be attributed to the fact that the electrostatic interaction of sodium titanate on the surface with the ions in the water is similar to the process which occurs in the SBF [56]. That is, the sodium titanate releases Na^+ ions by exchange with H_3O^+ ions in the water to form Ti–OH

Fig. 5 continued



groups on the surface. After intensive investigations into the mechanisms of calcium phosphate deposition, it is now widely accepted that the number of Ti–OH functional groups plays a determining role in the formation of bone-like apatite layers in the SBF [57, 58]. After the NaOH-treated and water-aged titanium metals are immersed in the SBF, the abundant Ti–OH groups are negatively charged [59–61] and can combine with the positively charged Ca^{2+} ions in the SBF. If there are enough Ti–OH groups on the surface of the Ti metal, the Ca^{2+} ions can continually accumulate on the surface with the result that it gradually gains an overall positive charge. As a result, the positively charged surface combines with negatively charged phosphate ions to form calcium phosphates. Thus, the calcium phosphates formed in this manner initially take on an amorphous structure but subsequently transform into more stable crystalline apatites [60, 61].

According to the present results, while all samples of c.p. Ti and Ti–7.5Mo subjected to NaOH treatment and water aging show a greater calcium phosphate-forming ability than those without water aging, after 48 h of water treatment, samples did not show a further increase in calcium phosphate-forming ability, possibly due to a thinner sodium titanate layer (Fig. 2). This finding is also in agreement with the water-contact angles measured in this study (Fig. 5), which reached their lowest values after undergoing water aging for 24 h. This is further confirmed by Wang et al. [62] who also found that enrichment of Ti–OH groups increases the surface energy (by decreasing the contact angle) on the Ti surfaces.

The results of the EDS analysis of the NaOH-treated and water-aged surfaces after being soaked in SBF for 13 days are shown in Fig. 6. Under these conditions, all the specimens exhibited very intense peaks of Ca and P, although the intensities of these peaks were greater in the Ti–7.5Mo specimens than in the c.p. Ti. Moreover, the intensities of the Ti peaks were much lower for the Ti–7.5Mo subjected to water aging for 12 or 24 h and the c.p. Ti subjected to water aging for 24 h. This result could be due to the interference from the calcium phosphate deposits which appeared after soaking, thereby indicating that these coatings were thick enough to prevent the penetration of X-ray beams into the substrate surface.

The pH value of the SBF was found to increase gradually during the immersion of the NaOH-treated and water-aged metallic samples, thus indicating an increasing concentration of hydroxyl group (OH^-) ions. This pH approached peaks of about 7.45–7.52 on the first day for both the c.p. Ti and the Ti–7.5Mo samples which received the NaOH and water treatment. However, for samples which were not water-aged, the pH approached peaks of 7.48 on the second day, as shown in Fig. 7. This pH increase in the SBF occurs during dissolution due to the release of cations from the sodium titanate layer via an ion-exchange mechanism with protons (H^+/H_3O^+) in the solution [63]. During immersion in SBF, the pH values reached their maximum after either 1 or 2 days, and subsequently decreased with further soaking, thus implying that a continuous precipitation of the bone-like apatite layer would occur thereafter. In the present experiment, the calcium phosphates began to deposit on NaOH- and water-treated substrates within 1 day after immersion in the SBF, which corresponds with the peak pH value attained on the first day. By contrast, in our previous study [39], the calcium phosphates began to deposit on the non-water-aged samples on the third day after immersion, thereby corresponding with the peak pH value on the third day.

Throughout the period of immersion in SBF, all the titanium metals showed varying rates of weight gain, as shown in Fig. 8. These variations were due to the differential dissolution and precipitation rates of Ca and P. Once the calcium phosphate nucleation started, it was expected

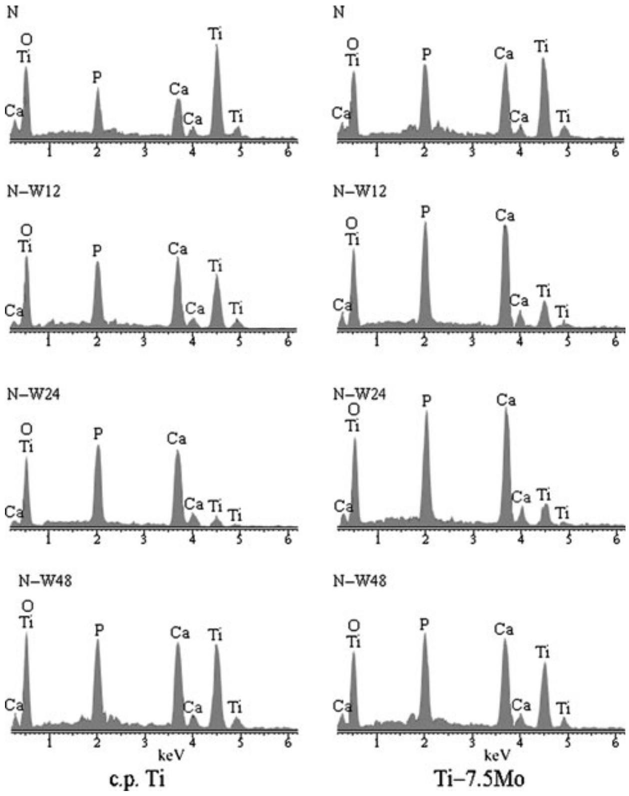


Fig. 6 EDS of NaOH-treated and subsequently water-aged c.p. Ti (*left side*) and Ti–7.5Mo (*right side*) after soaking in SBF for 13 days

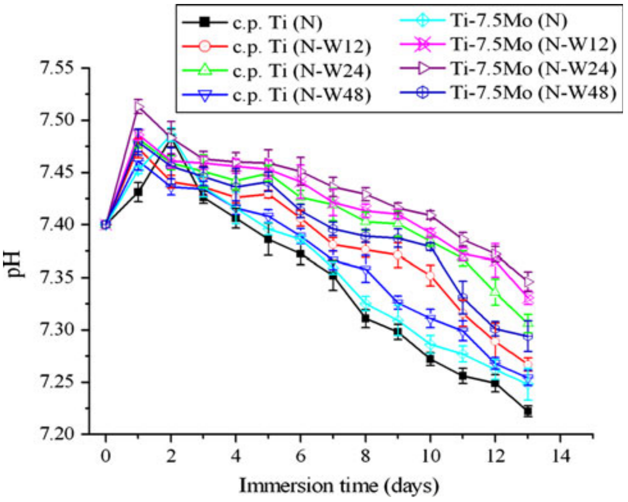


Fig. 7 pH values of SBF as functions of soaking time for c.p. Ti (cpT) and Ti–7.5Mo (TM) subjected to NaOH (N) or NaOH–water (N–W) treatments for 12, 24, or 48 h

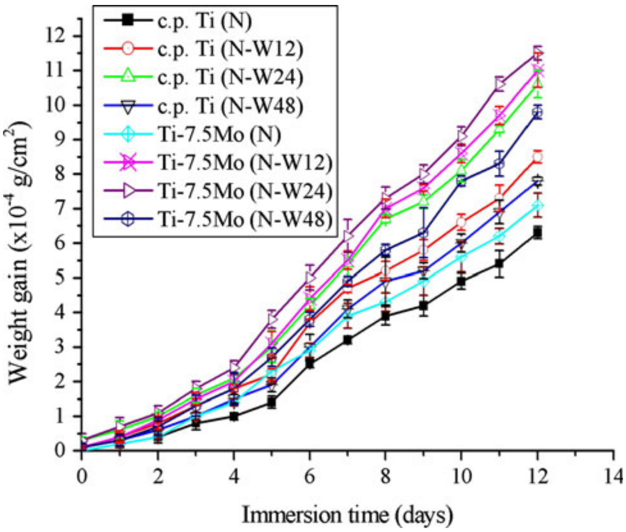


Fig. 8 Weight gain as functions of soaking time for c.p. Ti (cpT) and Ti–7.5Mo (TM) subjected to NaOH (N) or NaOH–water (N–W) treatments for 12, 24, or 48 h

that there would be consistent weight gain. In fact, the calcium phosphate deposits were greater for the water-aged c.p. Ti and Ti–7.5Mo samples than for their non-water-aged counterparts, as indicated in the measurements of weight gain (Fig. 8). Furthermore, the deposited amounts of calcium phosphates were much greater for the Ti–7.5Mo after water aging for 12 and 24 h than for all other conditions. These results are also consistent with the observations recorded elsewhere in this report, as indicated in the results from SEM (Fig. 5) and EDS (Fig. 6).

Conclusions

In this study, c.p. Ti and Ti–7.5Mo were treated with NaOH, aged in water, and subsequently soaked in 1.5SBF to induce calcium phosphate coating formations on their surfaces. The effect of various water aging times on the calcium phosphate-forming ability of c.p. Ti and Ti–7.5Mo was also evaluated. The results obtained in this research may be summarized as follows:

(1) Sodium titanate ($Na_2Ti_5O_{11}$) reaction layers appeared on all c.p. Ti and Ti–7.5Mo samples after NaOH treatment. The Ti–7.5Mo had a thicker layer than the c.p. Ti under the same conditions.

(2) NaOH treatments of c.p. Ti and Ti–7.5Mo enhanced their surface wettability, and the water-contact angles of the surfaces were further reduced as the c.p. Ti and Ti–7.5Mo substrates were subsequently aged in water. The contact angles measured after 24 h were the lowest, being less than 9° for c.p. Ti and less than 6° for Ti–7.5Mo.

(3) There was no new particle formation on the surfaces of c.p. Ti and Ti–7.5Mo after only NaOH treatment and subsequent soaking in 1.5SBF solution for 1 day. However, numerous nucleation spheres and deposition formed on the surfaces of both substrates treated with both NaOH and water for the same soaking time. Most importantly, higher calcium phosphate-forming ability can evidently be acquired by subsequent water aging, especially for durations of 12 and 24 h for Ti–7.5Mo and 24 h for c.p. Ti.

(4) Of all test conditions, the deposited amounts of calcium phosphates were the greatest for Ti–7.5Mo after NaOH treatment and subsequent water aging for 12 or 24 h. The results also indicated that the deposited amounts of calcium phosphates were much greater for pre-treated Ti–7.5Mo than for pre-treated c.p. Ti under the same conditions.

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