

# A protocol to develop crack-free biomimetic coatings on Ti6Al4V substrates

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(Received 22 November 2006; accepted 16 February 2007)

Biomimetic coating of titanium and related alloys with carbonated apatitic calcium phosphate is an important area of research in implantology. While this paper specifically refers to coating Ti6Al4V, the results are valid with other related alloys as well. One step in the protocol involves an intermediate alkali treatment of Ti6Al4V to form a sodium titanate layer on the alloy surface. This pretreatment enhances the formation of the coating from simulated body fluid (SBF) solutions. Many papers in the biomimetic coating literature demonstrate the presence of cracks in coatings, irrespective of the SBF compositions and placement of the substrates. The presence of cracks may result in degradation and delamination of coatings. To the best of our knowledge, this issue remains unresolved. Therefore, the aim of this study was: (i) to examine and understand the reasons for cracking and (ii) based on the results, to develop a protocol for producing crack-free apatitic calcium phosphate coatings on Ti6Al4V substrates. In this study, the authors focused their attention on the alkali treatment procedure and the final drying step. It is hypothesized that these two steps of the process affect the crack formation the most. In the first case, the surfaces of alkali-treated substrates were examined with/without water-soaking treatment before immersing in SBF. This water treatment modifies the sodium titanate surface layer. In the second case, two different drying techniques (after soaking in SBF) were used. In one procedure, the coated substrates were dried rapidly, and in the other they were dried slowly. It was observed that the water treatment, irrespective of the drying method, provides a surface, which on subsequent soaking in SBF forms a crack-free apatitic calcium phosphate coating. Based on these results, the authors suggest a protocol incorporating a water-soaking treatment after the alkali treatment and prior to the SBF soaking treatment to obtain crack-free coatings.

## I. INTRODUCTION

Coating titanium and its alloys with carbonated apatitic calcium phosphate layer has been of increasing interest due to its ability to directly bond with bone.<sup>1,2</sup> Of the many coating processes available today, the biomimetic coating technique has many advantages including producing carbonated apatitic calcium phosphate coatings, which is otherwise impossible to produce. The coatings are formed by soaking an alkali pretreated titanium (or an alloy) substrate in a simulated body fluid (SBF) solution.<sup>3-6</sup> The alkali pretreatment is a crucial step; it

forms a hydrous sodium or potassium titanate layer (depending upon the alkali used) on the substrate.<sup>3-6</sup> The as-formed sodium (or potassium) titanate on soaking in SBF exchanges Na<sup>+</sup> (K<sup>+</sup>) ions with the H<sub>3</sub>O<sup>+</sup> ions and forms Ti-OH groups on the surface that increases the ionic activity of apatite in SBF.<sup>7</sup> During soaking, nanometer-sized apatitic calcium phosphate globules rapidly nucleate on the sodium (or potassium) titanate layer and then grow to a few microns by consuming Ca and P ions from the SBF solution.<sup>4</sup>

Despite all the advantages of the biomimetic coating process, the phenomenon of cracking persists. Furthermore, the reason for cracking of such coatings remains unresolved. The present paper is an attempt to examine this issue. Previously, the present authors investigated the apatite-inducing abilities of different SBF solutions

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DOI: 10.1557/JMR.2007.0193

referred to as *c*-SBF, *t*-SBF, and *r*-SBF on these alkali-treated titanium substrates.<sup>8</sup> *c*-<sup>9</sup> and *r*-SBF<sup>10,11</sup> are conventional and revised versions of SBF, as developed by Kokubo. *t*-SBF is the formulation developed by Tas.<sup>12,13</sup> The compositions of the three SBF solutions and the important differences between them are given in Ref. 8. The authors noted that cracks were persistently present on these apatitic calcium phosphate coating irrespective of the composition of the coating solution.<sup>8</sup> Also, the placement of the substrates (e.g., horizontal or vertical) was examined as a parameter affecting the formation of cracks in the coatings.<sup>8</sup> These cracks were present on all the substrates irrespective of their placements.<sup>8</sup> A major consequence of the presence of these cracks substantially increases the chances of delamination, thereby decreasing the coating's ability to bond with the natural bone.

The scanning electron micrographs, as reported by the present authors<sup>8</sup> and other researchers,<sup>14–22</sup> indicate that these cracks are not just surface cracks and are rather deep. However, in Refs. 14 to 20 the authors did not mention the cause of these deep cracks. In other papers, drying is cited as a potential reason for their formation.<sup>6,8,21,22</sup> The main reason for this argument is that the entrapped water does not readily escape during low-temperature drying and leads to deep cracks.<sup>6,8,21,22</sup> It is known that in the SBF solution, Posner's clusters are the dominant transient phase during the formation of calcium-deficient carbonated calcium phosphates.<sup>23–25</sup> Since Posner's clusters already have water molecules in their intercluster spaces, the aggregates of these clusters forming the nanoporous coating layers on Ti6Al4V surfaces also entrap a sizable amount of water.<sup>23–25</sup> Yet another explanation is attributed to the presence of thermal expansion coefficient mismatch between the Ti6Al4V substrates and the calcium phosphate coating layers.<sup>26</sup> Most of these explanations are hypothetical in nature and are not based on concrete experimental results.

The broad objective of the present work was to find the reasons for the formation of such cracks and to establish a protocol for producing crack-free homogeneous biomimetic coating on Ti6Al4V utilizing *t*-SBF. The reasons for using *t*-SBF are given in Ref. 7. Since the cracks appear to be deep, the authors hypothesize that the hydrous sodium titanate layer<sup>4</sup> formed on the Ti6Al4V substrate has a role in the formation of cracks in the coatings. Thus in this careful study, we modified the pretreatment procedure and subsequently examined its effect on formation of cracks in the coatings. Also, we attempted new drying procedures to examine the effect of drying on the crack formation. The rate of removal of water differentiates the new and the conventionally used procedures. The new procedure leads to the rapid removal of water compared with the conventional method, in which the entrapped water does not readily escape.

## II. EXPERIMENTAL PROCEDURE

### A. Substrate preparation and alkali pretreatment

Ti6Al4V strips (Grade 5, McMaster-Carr, Atlanta, GA), with the dimensions of 10 mm × 10 mm × 1 mm, were used as substrates in the SBF coating. The substrates were first abraded with a #100 SiC paper (FEPA P#1000, Struers, Westlake, OH) and then washed three times with acetone, ethanol, and deionized water, respectively, in an ultrasonic bath. Each substrate was then immersed in 50 ml of 5 M NaOH solution at 60 °C for 24 h. At the end of this alkali treatment, substrates were given two different treatments to check the effect on change of composition of treated layer on coating cracks. The first treatment involved the most commonly used practice of drying the substrates at 40 °C for 24 h after alkali treatment. The second treatment consisted of immersing the substrates in water at room temperature (RT) for 24 h after the alkali treatment and then drying them at 40 °C for 24 h.

### B. SBF solution preparation

The details of SBF preparation routines are given in Table I. Freshly prepared *t*-SBF solution<sup>12,13</sup> was used in coating experiments. We concentrated the basic SBF recipe by 1.5 times, as per common practice in the biomimetic coating of Ti6Al4V. The order of addition of the reagents to 700 ml of water is given in the second column of Table I. A total of 65 ml of 1 M HCl was consumed for pH adjustments during the preparation of 1 l of 1.5 × *t*-SBF solution. A 15 ml aliquot of this acid solution was added just before the addition of the sixth reagent, CaCl<sub>2</sub>·2H<sub>2</sub>O. Otherwise, the solution would display slight turbidity. The remaining part of the HCl solution was used during the subsequent titration. Following the addition of the eighth reagent, tris(hydroxymethyl) aminomethane, the solution temperature was raised from ambient temperature to 37 °C. This solution was then titrated with 1 M HCl to a pH of 7.4 at 37 °C. During the titration process, the solution was also continuously diluted with consecutive additions of deionized water to make the final volume equal to 1 l.

TABLE I. Preparation of *t*-SBF solution (1 L)<sup>12,13</sup>

Order	Reagent	Weight (g)	Ion	Human plasma (mM)	SBF (mM)
1	NaCl	6.547	Na <sup>+</sup>	142	142
2	NaHCO <sub>3</sub>	2.268	Cl <sup>-</sup>	103	125
3	KCl	0.373	HCO <sub>3</sub> <sup>-</sup>	27	27
4	Na <sub>2</sub> HPO <sub>4</sub> ·2H <sub>2</sub> O	0.178	K <sup>+</sup>	5	5
5	MgCl <sub>2</sub> ·6H <sub>2</sub> O	0.305	Mg <sup>2+</sup>	1.5	1.5
6	CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.368	Ca <sup>2+</sup>	2.5	2.5
7	Na <sub>2</sub> SO <sub>4</sub>	0.071	HPO <sub>4</sub> <sup>2-</sup>	1	1
8	(CH <sub>2</sub> OH) <sub>3</sub> CNH <sub>2</sub>	6.057	SO <sub>4</sub> <sup>2-</sup>	0.5	0.5

### C. Coating and drying process

For coating purposes, the pretreated substrates were soaked vertically in 100 ml of *t*-SBF at 37 °C in tightly sealed Pyrex bottles of 100 ml capacity for a period of 7 days. The reason for using vertical placement (by hanging in the solution bottle via a stainless steel wire) is given in Ref. 7. The SBF solution was replenished at every 48 h. Prior to replenishment, fresh SBF solutions of pH 7.4 were heated to 37 °C. The substrates were removed from the SBF solution followed by gentle washing with approximately 100 ml deionized water and then dried using two different techniques. The first technique involved the commonly used method for drying the biomimetically coated substrates that is, drying the substrates at 40 °C for 24 h. The second technique involved water soaking, followed by rinsing with 50 ml of 99.5% ethanol and then placing the substrates at RT for 15 min to evaporate ethanol.

### D. Sample characterization

For phase analysis, the surfaces of the uncoated and coated substrates were investigated by x-ray diffraction (XRD, XDS 2000, Scintag Corp., Sunnyvale, CA) using monochromated Cu K $\alpha$  radiation generated at a voltage and power of 40 kV and 30 mA, respectively. The substrates were also analyzed by using Fourier-transformed infrared (FTIR) spectroscopy (Nicolet 550, Thermo-Nicolet, Woburn, MA). FTIR was equipped with an Endurance Foundation Series single-bounce diamond ATR (50° incidence angle), and 32 scans were performed at a resolution of 4 cm<sup>-1</sup>. To analyze the substrate surface, before and after every treatment for cracks, scanning electron microscope (SEM, S-4700, Hitachi Corp., Tokyo, Japan) operated at 5 kV was used. To determine the amount of sodium present in the surface layer, samples were characterized using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Model 61E, Thermo Electron, Madison, WI).

## III. RESULTS

The results of this study are divided into two groups: (i) an alkali pretreatment before soaking in SBF solution and (ii) a drying step after soaking in SBF solution.

### A. Alkali pretreatment before soaking in SBF solution

After the alkali treatment, substrates were divided in two sets of samples; the first set was oven dried at 40 °C for 24 h, and the second set was soaked in water and then oven dried at 40 °C for 24 h. After completing these procedures, the substrates were examined by XRD, FTIR, and SEM. Figure 1 shows the XRD patterns of (a) as-received Ti6Al4V substrates, (b) substrates after pol-

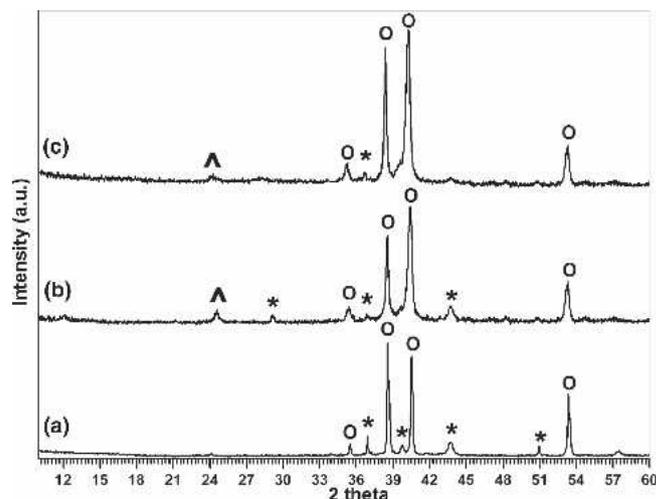


FIG. 1. XRD pattern of (a) as-received Ti6Al4V, (b) 5 M NaOH treated and then dried at 40 °C, and (c) 5 M NaOH treated and then soaked in water (O: titanium; \*: rutile; and ^: sodium titanate).

ishing, NaOH-treatment, and drying at 40 °C for 24 h, and (c) substrates after polishing, NaOH treatment, water treatment, and then drying at 40 °C for 24 h. Ti6Al4V readily forms titanium oxide (TiO<sub>2</sub>) layer on the surface on exposure to air. Prior to any treatment, titanium oxide was present on the as-received Ti6Al4V strips of this study as determined by the XRD pattern shown in Fig. 1(a). All rutile (TiO<sub>2</sub>) peaks are marked as (\*) on the pattern. A hydrated layer of sodium titanate (marked as ^) and titanium oxide (rutile, TiO<sub>2</sub>) was reported to form on the exposed surfaces of Ti6Al4V strips after 24 h of immersion in a 5 M NaOH solution at 60 °C.<sup>3,4,16</sup> This layer was indeed found to be present on both NaOH-treated and water-treated Ti6Al4V strips. Both the patterns have similar peaks and respective intensities, and no significant difference was found in the XRD patterns [Figs. 1(a) and 1(b)]. The FTIR pattern of NaOH-treated Ti6Al4V strips [Fig. 2(b)] shows that they were hydrated in nature with a huge band of H<sub>2</sub>O present from 3700–2400 cm<sup>-1</sup> and one present at 1640 cm<sup>-1</sup>. Both of these bands were also present on the substrates after water treatment [Fig. 2(c)], thus, confirming their hydrated nature. The most important difference in the FTIR pattern was the presence of carbonate bands (CO<sub>3</sub><sup>2-</sup>) between 1470 and 1410 and at 870 cm<sup>-1</sup> in the NaOH-treated substrates [Fig. 2(b)], whereas these bands were absent after water treatment [Fig. 2(c)] as shown. Inductively coupled plasma analyses showed significant differences in the amount of Na present on the surface layer of the NaOH-treated and water-treated samples. As expected during water treatment, sodium was released from the substrate surface into the water in which they were immersed. The amount of Na present in the hydrous sodium titanate layer

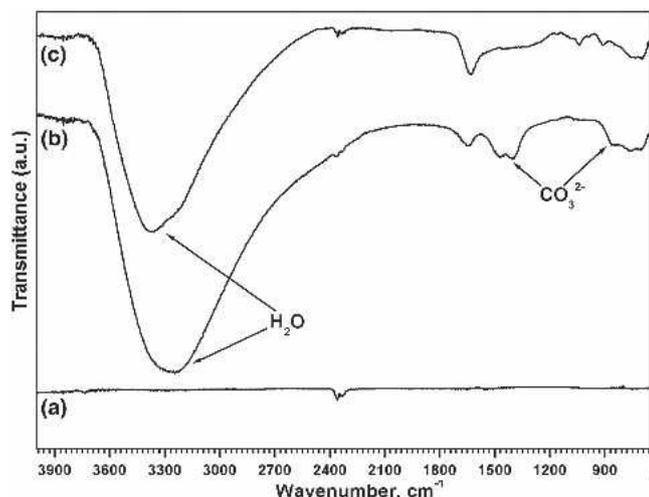


FIG. 2. FTIR pattern of (a) as-received Ti6Al4V, (b) 5 M NaOH treated and then dried at 40 °C, and (c) 5 M NaOH treated and then soaked in water (arrows point to the H<sub>2</sub>O and CO<sub>3</sub><sup>2-</sup> bands).

of NaOH-treated substrates was 8.25 wt%, whereas, in water-treated substrates, the amount decreased to 3.6 wt%.

Examination of these differently treated substrates under the SEM also showed variations in microstructure. The alkali treatment, prior to soaking in SBF solution, provided the substrate with a certain nanoscale roughness, as shown in the SEM micrographs of Fig. 3(a). The nanoporous structure formed by the NaOH treatment was unchanged after water treatment [Fig. 3(b)]. However, the water treatment had a considerable effect on the microstructure. The NaOH-treated substrates that were dried at 40 °C subsequently showed a large number of cracks [Fig. 3(a)], which were persistent throughout the surface of the hydrated sodium titanate layer. These cracks might have formed during the drying process at 40 °C due to the release of either water or carbonates from the layer. However, cracks could not be seen in the low-magnification micrographs (inset in Fig. 3), only in the high-magnification micrographs do they (cracks) become detectable. In contrast, the water-treated substrates were crack-free, as shown in Fig. 3(b). To summarize, it is clear that water soaking after alkali treatment forms a hydrate sodium titanate layer without carbonates and cracks, and with a lower sodium content. All other features remain the same.

### B. Drying step after soaking in SBF solution

This section describes the results obtained after the alkali-treated substrates (with/without water treatment) were soaked in 1.5 times *t*-SBF solution. Upon soaking, calcium phosphates covered the surface of these substrates within 7 days (Fig. 4). The alkali-treated substrates with/without water treatment after a SBF coating were dried in two different methods to see the effect of

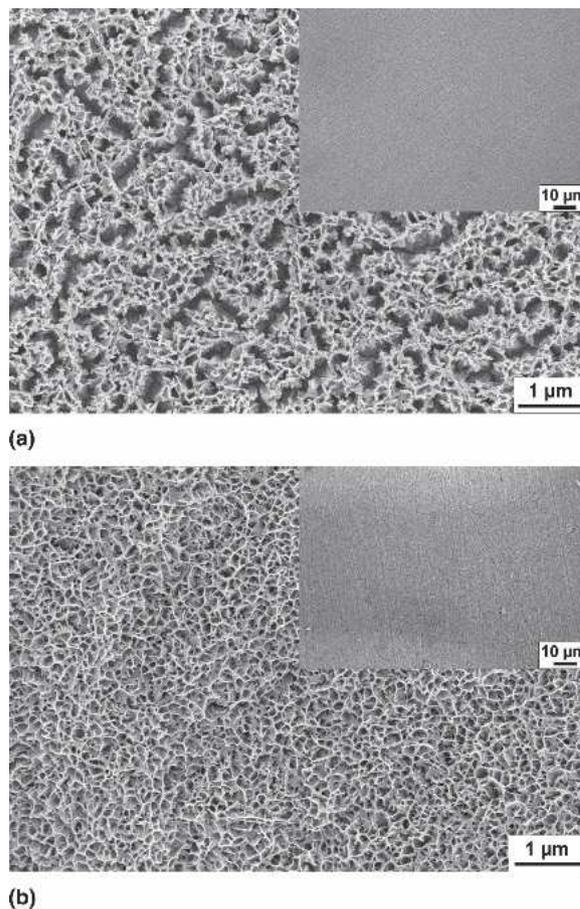


FIG. 3. SEM micrographs of Ti6Al4V strips treated with 5 M NaOH at 60 °C for 24 h then (a) dried at 40 °C for 24 h, and (b) soaked in deionized water for 24 h (inset shows low magnification view).

kinetics of drying. One method was to dry the substrates by placing them at 40 °C for 24 h; and the other was to wash the coated substrates with ethanol and then dry them at room temperature. The former method is slower than the latter. Figure 4(a) shows that the NaOH-treated substrate coated with apatitic calcium phosphate developed deep cracks after drying at 40 °C for 24 h. Because these cracks have previously been referred to as “drying cracks,” or those formed while drying, the second method of drying was used. The SEM micrographs [Fig. 4(b)] showed morphology and cracks similar to those shown in Fig. 4(a). Thus, this ethanol treatment was unsuccessful in removing the cracks from the coating surface. Figures 4(c) and 4(d) show the substrates that were water treated after alkali treatment and then soaked in SBF for 7 days. Subsequently, the substrates were washed with water and then dried at 40 °C for 24 h [shown in Fig. 4(c)]. The SEM micrographs at both high and low magnification (shown in inset) show a crack-free coating surface and also show no significant difference in the morphology of the apatitic calcium phosphate coatings. The micrograph depicts round globules with

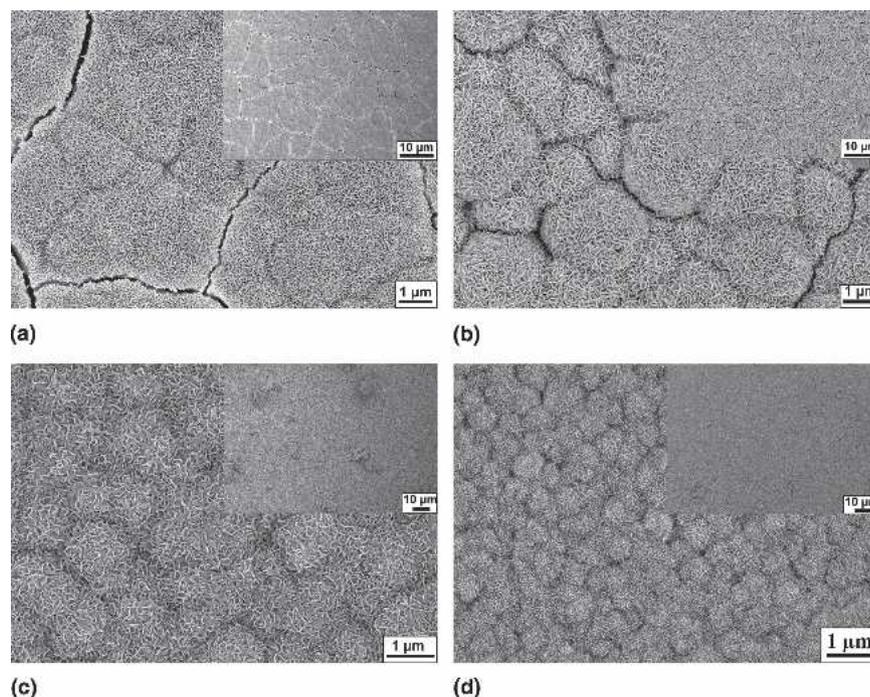


FIG. 4. Substrates after alkali treatment dried at 40 °C for 24 h, then soaked in *t*-SBF for 7 days and then (a) dried at 40 °C for 24 h and (b) dried with ethanol. Substrates after alkali treatment were soaked in deionized water for 24 h, soaked in *t*-SBF for 7 days, and then (c) dried at 40 °C for 24 h, and (d) dried with ethanol (inset shows low-magnification view).

needlelike intermingled nanosize calcium phosphates on the surface of Ti6Al4V strips. At the end of the soaking time, the substrates [shown in Fig. 4(d)] were first washed with water and then rinsed with ethanol. The micrograph is very similar to that in Fig. 4(c), which also shows a crack-free apatitic calcium phosphate coating.

The calcium phosphate coatings formed on substrates after different pretreatments retained a similar XRD pattern (Fig. 5). The broadening of the 211, 112, and 300 reflections between 30° and 34°, and the relatively high

intensity of the 002 reflection at 25.9° confirms the nanonature and the low crystallinity of the coatings. The titanium peaks were still visible and these are marked as (\*) in the XRD pattern (Fig. 5). FTIR patterns (Fig. 6) were also similar for all coated samples and showed that all the coatings consisted of carbonated ( $\text{CO}_3^{2-}$  ion absorption bands seen at 1470–1420 and 875  $\text{cm}^{-1}$ ) calcium phosphates. The absence of the stretching and vibrational modes of the O–H group at 3571 and 639  $\text{cm}^{-1}$  confirmed that these coatings might not be simply termed as

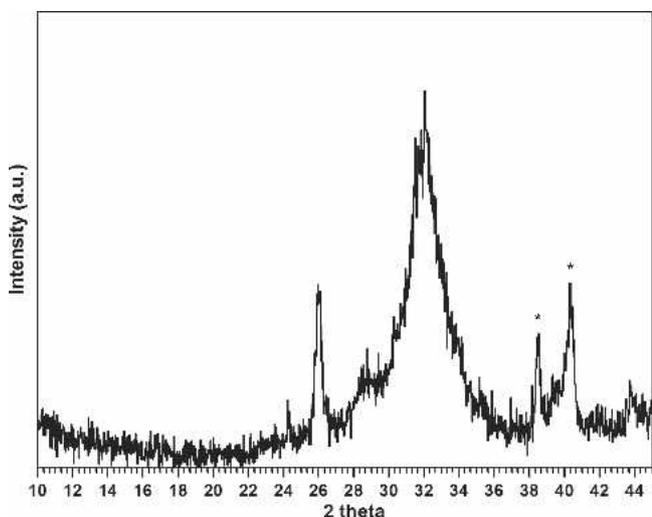


FIG. 5. XRD pattern of alkali-treated Ti6Al4V soaked in  $1.5 \times t$ -SBF for 7 days.

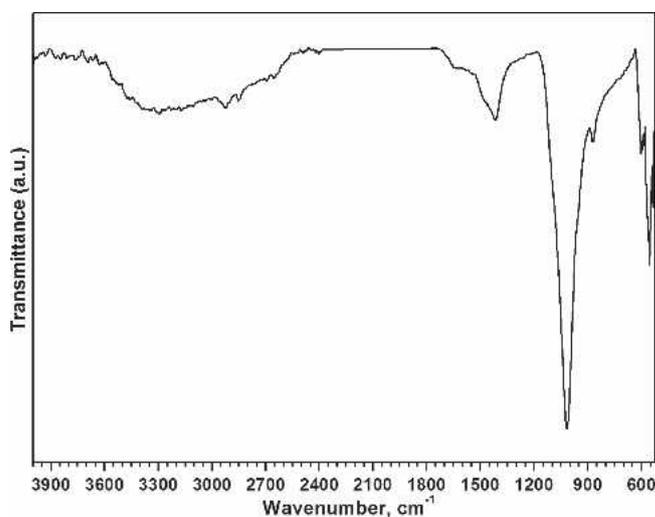
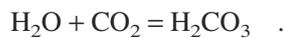


FIG. 6. FTIR pattern of alkali-treated Ti6Al4V soaked in  $1.5 \times t$ -SBF for 7 days.

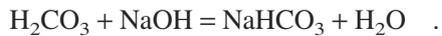
hydroxyapatite. These characteristics are similar to the coatings that we came across in our earlier experiments.<sup>8</sup> Thus, the coatings retain all the expected characteristics, but remain crack-free when soaked in water after alkali treatment.

#### IV. DISCUSSION

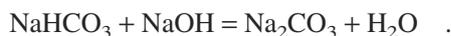
The deionized water, which normally has a neutral pH of 7.0, now has an acidic pH of approximately 5.7 when exposed to air. Carbon dioxide dissolves slightly in water to form carbonic acid,  $\text{H}_2\text{CO}_3$ , a weak acid, according to the reaction:



When sodium hydroxide is added to this deionized water, some of it reacts with the carbonic acid to form sodium bicarbonate:



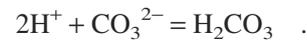
The pH of the solution is increased to nine. The bicarbonate ion is relatively unstable in comparison to the carbonate ion at this pH. Thus, it leads to the formation of sodium carbonate, as per:



Thus, the alkali solution now contains mostly NaOH with small amounts of dissolved  $\text{Na}_2\text{CO}_3$ . The mechanism of the reaction of the titanium alloy with this alkaline solution has been previously explained by Kokubo et al.<sup>4</sup> On soaking the substrates in alkali solution, the negatively charged hydrated titanate forms, with incorporated sodium ions in it.<sup>4</sup> A hydrated layer of sodium titanate and titanium oxide has been reported to form on the exposed surfaces of Ti6Al4V strips after 24 h of immersion in a 5 M NaOH solution at 60 °C.<sup>3,4,16</sup> The formation of this hydrous sodium titanate after alkali treatment was confirmed by the XRD pattern, as shown in Fig. 1. Since this solution contains small amounts of  $\text{Na}_2\text{CO}_3$ , it also plays a role in the etching process of the Ti6Al4V strips. There is a tendency to form either a compound containing carbonates in it or a complex with sodium titanate on the surface layer. Although no additional phase was detected by XRD, the presence of carbonates in the treated surface is confirmed by the FTIR pattern, as shown in Fig. 2(b). To summarize, it is clear that the surface layer of NaOH-treated Ti6Al4V consists of a mixture of hydrated, carbonated sodium titanate and titanium dioxide (rutile).

One possible explanation can be presented when the alkali-treated substrates were immersed in deionized water for 24 h at RT. The deionized water has a pH of 5.7, at which carbonic acid is the most stable ion phase. On soaking the NaOH-treated substrates in deionized water, there is a tendency for the  $\text{CO}_3^{2-}$  ions present in the

surface layer to react with the  $\text{H}^+$  ions of water and form carbonic acid:



After 24 h of soaking time, all the carbonates from the substrate surface go through the reaction. After drying, the substrate is a carbonate-free surface. This effect of carbonate release from the surface with water treatment is substantiated by the FTIR pattern shown in Fig. 2(c). Thus, the data presented in this study highlight differences in the compositions of surface layers after two different surface treatments. The data show that the substrates, before and after water treatment, differ in the (i) sodium and (ii) carbonate contents in the surface-treated layer.

The water-soaking treatment leads to a decrease in the amount of sodium in the alkali-treated layer from 8.25 to 3.6 wt%. In the present study, the water treatment was performed in large amounts of water for 24 h at RT. Though performing the water-soaking treatment with a small quantity of water at RT for 1 min results in a decrease in the amount of sodium, it does not remove the carbonates from the surface. Jonasova et al.<sup>17</sup> studied the effect of washing the alkali-treated substrates with water at RT on their apatite-inducing ability. No significant difference in the rate of apatite formation was observed but the Na amount was lowered from 9.6 to 3.5 at.%.<sup>17</sup> When the water treatment is performed with large amounts of water for 48 h at 80 °C, Uchida et al.<sup>27</sup> observed an increase in apatite formation on titanium metal. However, this enhancement of the apatite-forming ability is due to the formation of anatase, formed from the conversion of sodium titanate gel after water treatment at high temperatures.<sup>27</sup> The decrease in sodium content in the surface layer did not cause this increase. Since we performed the water treatments at RT, our results were in direct correlation to those obtained by Jonasova et al.<sup>17</sup> SEM micrographs in Fig. 4 show that the rate of apatite formation is similar on substrates with different Na content. XRD results (Fig. 1) confirm that the substrate surface consists of rutile after water treatment at RT, instead of anatase as formed by Uchida et al.<sup>27</sup> after water treatment at 80 °C.

In studies performed by Jonasova et al.<sup>17</sup> and Uchida et al.,<sup>27</sup> cracks were persistently present in all the biomimetically deposited coatings. These findings show that the presence of different sodium content in the surface layer prior to soaking in SBF solution does not play a role in the formation of cracks in the apatitic calcium phosphate layer. Rather, it indicates that the phases present on the alkali-treated layer are more important parameters than sodium content for producing crack-free apatitic calcium phosphate coatings.

It is important to emphasize that the SEM micrographs

(Fig. 4) in this present study show significant differences in terms of crack formation on the apatitic calcium phosphate layer. Cracks were observed on the calcium phosphate layer deposited on the substrate containing 8.25 wt% Na [Figs. 4(a) and 4(b)], whereas none were observed after soaking in SBF on the substrate previously containing 3.6 wt% Na [Figs. 4(c) and 4(d)]. The substrate surfaces both before and after water treatment contain sodium titanate and rutile. No other phase (e.g., anatase) was detected by the XRD. Since we rule out the possibility of the sodium contents affecting the crack formation, we can conclude that carbonate must play an important role in crack formation. The role of carbonates in forming cracks initially becomes visible just after the alkali treatment. The SEM micrograph in Fig. 3(a) shows the NaOH-treated substrate without water treatment and also demonstrates a multitude of cracks on the sodium titanate surface. This is possibly due to the presence of (i) water, as these substrates are hydrated in nature, and (ii) carbonates, as the FTIR pattern in Fig. 2(b) confirms their presence. Significant differences are observed in the SEM micrographs after water treatment as no cracks are seen on the sodium titanate layer [Fig. 3(b)]. The FTIR pattern in Fig. 2(c) shows that the substrate is hydrated in nature and has no carbonate bands present. Thus, the presence of cracks in the alkali-treated substrates occurring while drying is due to possible loss of carbonates as CO<sub>2</sub> to the air. Since no carbonates were present in the water-treated Ti6Al4V strips, no cracks were observed on the sodium titanate layer.

These substrates with/without cracks and with/without carbonates are soaked in SBF solution. During the final drying step, coatings with underlying carbonated titanate phase end up cracking because the carbonates are released from them. These cracks substantially increase the likelihood of delamination, thereby decreasing the implant's bonding ability to natural bones. Thus, the water-soaking step is expected to improve the performance of coated Ti (or alloy) implants.

## V. CONCLUSIONS

This paper presents results leading to the cause of crack formation in biomimetically coated Ti6Al4V strips. By performing carefully planned experiments, it was found that carbonates are present in the sodium titanate layer formed during the pretreatment of the substrates. These carbonates during drying tend to evaporate from the underlying surface layer as CO<sub>2</sub>, and thus deep cracks form. Successful removal of carbonates from this surface layer was performed by incorporating a water-soaking treatment prior to SBF soaking. Once the carbonates are removed, cracks cannot form during any subsequent drying step. This paper suggests a step in the protocol, which should be incorporated into the biomimetic coating process of titanium and related alloy substrates, to obtain crack-free coatings.

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## ACKNOWLEDGMENT

This work was supported by the Bishop Endowment and National Science Foundation Grant No. 0409119.

## REFERENCES

1. W-Q. Yan, T. Nakamura, K. Kawanabe, S. Nishigochi, M. Oka, and T. Kokubo: Apatite layer-coated titanium for use as bone bonding implants. *Biomaterials* **18**, 1185 (1997).
2. W-Q. Yan, T. Nakamura, M. Kobayashi, H-M. Kim, F. Miyaji, and T. Kokubo: Bonding of chemically treated titanium implants to bone. *J. Biomed. Mater. Res.* **37**, 267 (1997).
3. P. Li, I. Kangasniemi, K. de Groot, and T. Kokubo: Bone-like hydroxyapatite induction by a gel-derived titania on a titanium substrate. *J. Am. Ceram. Soc.* **77**, 1307 (1994).
4. T. Kokubo, F. Miyaji, H-M. Kim, and T. Nakamura: Spontaneous formation of bone-like apatite layer on chemically treated titanium metals. *J. Am. Ceram. Soc.* **79**, 1127 (1996).
5. H-M. Kim, F. Miyaji, T. Kokubo, and T. Nakamura: Apatite forming ability of alkali-treated Ti metal in body environment. *J. Ceram. Soc. Jpn.* **105**, 111 (1997).
6. A.C. Tas and S.B. Bhaduri: Rapid coating of Ti6Al4V at room temperature with a calcium phosphate solution similar to 10× simulated body fluid. *J. Mater. Res.* **19**, 2742 (2004).
7. H. Takadama, H-M. Kim, T. Kokubo, and T. Nakamura: TEM-EDX study of mechanism of bonelike apatite formation on bioactive titanium metal in simulated body fluid. *J. Biomed. Mater. Res.* **57**, 441 (2001).
8. S. Jalota, S.B. Bhaduri, and A.C. Tas: Effect of carbonate content and buffer used in SBF solutions on calcium phosphate formation on Ti6Al4V. *J. Mater. Sci. Mater. Med.* **17**, 697 (2006).
9. T. Kokubo: Surface chemistry of bioactive glass-ceramics. *J. Non-Cryst. Solids* **120**, 138 (1990).
10. A. Oyane, K. Onuma, A. Ito, H-M. Kim, T. Kokubo, and T. Nakamura: Formation and growth of clusters in conventional and new kinds of simulated body fluids. *J. Biomed. Mater. Res.* **64A**, 339 (2003).
11. H-M. Kim, K. Kishimoto, F. Miyaji, T. Kokubo, T. Yao, Y. Suetsugu, J. Tanaka, and T. Nakamura: Composition and structure of apatite formed on organic polymer in simulated body fluid with a high content of carbonate ion. *J. Mater. Sci. Mater. Med.* **11**, 421 (2000).
12. D. Bayraktar and A.C. Tas: Chemical preparation of carbonated calcium hydroxyapatite powders at 37 °C in urea-containing synthetic body fluids. *J. Eur. Ceram. Soc.* **19**, 2573 (1999).
13. A.C. Tas: Synthesis of biomimetic Ca-hydroxyapatite powders at 37 °C in synthetic body fluids. *Biomaterials* **21**, 1429 (2000).
14. H-M. Kim, H. Takadama, F. Miyaji, T. Kokubo, S. Nishiguchi, and T. Nakamura: Formation of bioactive functionally graded structure on Ti6Al4V alloy by chemical surface treatment. *J. Mater. Sci. Mater. Med.* **11**, 555 (2000).
15. F. Barere, C.A. van Blitterswijk, K. De Groot, and P. Layrolle: Influence of ionic strength and carbonate on the Ca-P coating formation from SBF X 5 solution. *Biomaterials* **23**, 1921 (2002).
16. M. Wei, H-M. Kim, T. Kokubo, and J.H. Evans: Optimizing the bioactivity of alkaline-treated titanium alloy. *Mater. Sci. Eng., C* **20**, 125 (2002).
17. L. Jonasova, F.A. Muller, A. Helebrant, J. Strnad, and P. Greil:

- Hydroxyapatite formation on alkali-treated titanium with different content of Na<sup>+</sup> in the surface. *Biomaterials* **23**, 3095 (2002).
18. S. Nishiguchi, S. Fujibayashi, H-M. Kim, T. Kokubo, and T. Nakamura: Biology of alkali- and heat-treated titanium implants. *J. Biomed. Mater. Res.* **67A**, 26 (2003).
  19. T. Kokubo, H-M. Kim, M. Kawashita, and T. Nakamura: Bioactive metals: Preparation and properties. *J. Mater. Sci. Mater. Med.* **15**, 99 (2004).
  20. L. Jonasova, F.A. Muller, A. Helebrant, J. Strnad, and P. Greil: Biomimetic apatite formation on chemically treated titanium. *Biomaterials* **25**, 1187 (2004).
  21. P. Habibovic, F. Barrère, C.A. van Blitterswijk, K. de Groot, and P. Layrolle: Biomimetic hydroxyapatite coating on metal implants. *J. Am. Ceram. Soc.* **85**, 517 (2002).
  22. S. Bharati, M.K. Sinha, and D. Basu: Hydroxyapatite coating by biomimetic method on titanium alloy using concentrated SBF. *Bull. Mater. Sci.* **28**, 617 (2005).
  23. X. Yin and M.J. Stott: Biological calcium phosphates and Posner's cluster. *J. Chem. Phys.* **118**, 3717 (2003).
  24. K. Onuma and A. Ito: Cluster growth model for hydroxyapatite. *Chem. Mater.* **10**, 3346 (1998).
  25. G. Treboux, P. Layrolle, N. Kanzaki, K. Onuma, and A. Ito: Existence of Posner's cluster in vacuum. *J. Phys. Chem. A* **104**, 5111 (2000).
  26. J.M. Gomez-Vega, E. Saiz, A.P. Tomsia, T. Oku, K. Suganuma, G.W. Marshall, and S.J. Marshall: Novel bioactive functionally graded coatings on Ti6Al4V. *Adv. Mater.* **12**, 894 (2000).
  27. M. Uchida, H-M. Kim, T. Kokubo, S. Fujibayashi, and T. Nakamura: Effect of water treatment on the apatite-forming ability of NaOH-treated titanium metal. *J. Biomed. Mater. Res.* **63**, 522 (2002).