

# RAPID COATING OF Ti6Al4V SURFACES USING A CALCIUM PHOSPHATE SOLUTION SIMILAR TO 10x SYNTHETIC BODY FLUID

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## ABSTRACT

This paper reports the utilization of high ionic strength ( $>1100$  mM) calcium phosphate solutions in the rapid deposition of carbonated apatitic calcium phosphates on Ti6Al4V surfaces within 2 to 6 hours, at room temperature.

The solution disclosed here multiplied the concentrations of calcium and phosphate ions in human plasma or synthetic (or simulated) body fluid (SBF) by a factor of ten. The solutions of this study did not contain any buffering agents, such as Tris or Hepes. Homogeneous formation of calcium phosphate (CaP) nano-clusters was observed, but their presence did not adversely affect the coating process. Solution pH was adjusted to 6.5 by adding proper amounts of solid  $\text{NaHCO}_3$  prior to the coating procedure. No  $\text{CO}_2$  bubbling was needed. Coating proceeded rapidly (2 to 6 h) with a linear rate. The adhesion strength of the coated layers was  $12 \pm 2$  MPa. The carbonate content (8 wt%) and Ca/P molar ratio (1.57) did qualify these coating as bonelike. The solution described here will especially be useful in coating, on an industrial-scale, the inner surfaces of the interconnected pores of metallic foams; i.e., trabecular metallic bone-substitutes.

## INTRODUCTION

SBF (synthetic or simulated body fluid) solutions, 2.5 mM  $\text{Ca}^{2+}$  and 1 mM  $\text{HPO}_4^{2-}$ , were shown [1-3] to induce apatitic CaP formation on metals, ceramics or polymers soaked in them. SBF solutions, in close resemblance to the Hanks Balanced Salt Solution (HBSS) [4], are prepared with the aim of simulating the ion concentrations present in the human plasma. Furthermore, to mimic human plasma, pH value of SBF solutions was adjusted to the physiological value of 7.4 by using organic buffers, such as Tris [3] or Hepes [5]. These compounds are not present in human plasma. The buffering agent Tris present in conventional SBF formulations, for instance, is reported [6] to form soluble complexes with several cations, including  $\text{Ca}^{2+}$ , which further reduces the concentration of free  $\text{Ca}^{2+}$  ions available for coating. Hepes, on the other hand, is rather unstable and easily loses a certain fraction of carbonate ions [7]. The hydrogencarbonate ion ( $\text{HCO}_3^-$ ) concentration in SBF solutions was kept between 4.2 mM (equal to that of HBSS) and 27 mM [1, 8].

However, nucleation and precipitation of calcium phosphates from either HBSS or SBF solutions are rather slow [9]. To get total surface coverage of a 10 x 10 x 1 mm titanium or titanium alloy substrate immersed into a 1.5 or 2 x SBF solution, one typically needs to wait for 2 to 3 weeks, with frequent (at every 36 to 48 hours) replenishment of the solution. The broad motivation in this work is to enhance the rate of CaP deposition.

In order to achieve the above objective, Barrere *et al.* [10] have developed unique 5 X SBF-like solution recipes (with pH values close to 5.8), which did not employ any Tris or Hepes. In that study [10], coating was achieved by employing two different solutions (solutions A and B as they referred), and pH was adjusted by continuous bubbling of CO<sub>2</sub> gas into the reaction chamber. A coating thickness of about 30 nm was achieved only after 6 h of immersion, which did not increase much even after 48 hours of further soaking, stirring and constant CO<sub>2</sub> bubbling at 50° C [10]. Moreover, they also introduced additional intermediate steps. These included [10] immersing the metal strips in the first 5 SBF solution (to seed the surface with calcium phosphate nuclei) for 24 h at 37° C, followed by another soaking in their second 5 SBF solution (to form the actual coat layers by a so-called growth process) for 6 to 48 h at 50° C [10]. There is yet another concern over the above-mentioned CO<sub>2</sub>-bubbling technique. Bubbling of CO<sub>2</sub> (with the sole purpose of maintaining the solution pH at around neutral values) results in calcium phosphate coatings with enormously increased carbonate ion concentrations [9].

The aim of this paper is to present the preparation of a new acidic solution, which contains 10 times the calcium and phosphate ion concentrations of human blood plasma. Such a solution, after raising its pH to around 6.5 by adding NaHCO<sub>3</sub>, should enhance the kinetics of coating formation even more. The resultant solution was able to coat Ti6Al4V strips at RT (22±1° C), in as little as 2 hours, and proven that it was not necessary to utilize 37° C and pH 7.4 conditions for coating purposes.

## EXPERIMENTAL PROCEDURE

Strips (or coupons) of Ti6Al4V were cut into typical dimensions of 10 x 10 x 0.20 mm and first abraded manually with a 1200-grit SiC paper. Strips were then cleaned with acetone, ethanol and deionized water, followed by etching each strip in 150 mL of a 5 M KOH solution at 60° C for 24 h, in a sealed glass bottle. Thoroughly rinsed (w/water) strips were finally heat-treated at 600° C for 1 h in Al<sub>2</sub>O<sub>3</sub> boats, with heating and cooling rates of 3° C/min.

Solution preparation recipe (for a total aqueous volume of 2 L) is given in Table 1. The chemicals given in Table 1 are added, in the order written, to 1900 mL of deionized water in a glass beaker of 3.5 L-capacity. Before the addition of the next chemical, the previous one was completely dissolved in water.

Reagent	Order	Amount (g)	Concentration (mM)
NaCl	1	116.8860	1000
KCl	2	0.7456	5
CaCl <sub>2</sub> ·2H <sub>2</sub> O	3	7.3508	25
MgCl <sub>2</sub> ·6H <sub>2</sub> O	4	2.0330	5
NaH <sub>2</sub> PO <sub>4</sub>	5	2.3996	10

Table 1 Stock solution preparation recipe (for a total volume of 2 L)

After all the reagents were dissolved, adding proper amount of water to reach pH 4.40 can be stored at RT, in a glass bottle to avoid precipitation.

Just prior to coating a Ti6Al4V strip, 10 mL of a 10 mM NaHCO<sub>3</sub> solution was added, and the pH of the solution was adjusted to around 6.5. The ionic strength of 1137.5 mM was maintained in a 250 mL glass bottle, which contained the Ti6Al4V strips for 2 to 6 hours during coating.

Samples were characterized by XPS, operated with Cu K<sub>α</sub> radiation at Nicolet 550, Thermo-Nicolet. For secondary electron mode, accelerated voltage was 10 kV. Thermo Jarrell Ash, Woburn, MA was used for SEM. For the SEM, the surfaces of the strips were coated with Au. Bonding strength of coatings to the substrates was tested by using a drop of glue (with a steel jigs 10 mm in diameter and 10 mm in height) to the substrates with an Instron 1130 (Instron, Roswell, GA) at a crosshead speed of 0.5 mm/min. The sample preparation technique was similar to the adhesion strength of bonelike coatings from SBFs of conventional recipes.

## RESULTS AND DISCUSSION

5 M KOH treatment applied to the surfaces. Figures 1a and 1b show the XPS spectra of those 5 M KOH + 600° C treated surfaces (Fig. 1a) belonged to a potassium phosphate (EDXS analyses). The surfaces of the strips were released into the solution (Fig. 1b) in the formation of a Ti-oxyhydroxide. The XPS spectra of the surfaces reacted with this basic layer are shown in Figure 1c.

The coating solution described above was prepared by the addition of NaHCO<sub>3</sub> to raise the pH of the solution monotonically (Fig. 2a). pH versus

After all the reagents were dissolved at RT, the solution was made up to 2 L by adding proper amount of water. This stable stock solution of pH value of 4.35-4.40 can be stored at RT, in a capped glass bottle, for several months without precipitation.

Just prior to coating a Ti6Al4V strip, a 200 mL portion of this stock solution was placed into a 250 mL-capacity glass beaker, and a proper amount of  $\text{NaHCO}_3$  powder (10 mM  $\text{HCO}_3^-$ ) was added, under vigorous stirring. Following the rapid dissolution of the  $\text{NaHCO}_3$ , the pH of the clear solution rose to 6.50 at RT. This solution (with an ionic strength of 1137.5 mM) was then transferred to a 250 mL-capacity glass bottle, which contained the Ti6Al4V strip inside, tightly capped and kept at RT for 2 to 6 hours during coating.

Samples were characterized by XRD (XDS 2000, Scintag Corp., Sunnyvale, CA; operated with  $\text{Cu}_{K\alpha}$  radiation at 40 kV and 30 mA), FTIR (Bruker, ATR-FTIR and Nicolet 550, Thermo-Nicolet, Woburn, MA), FE-SEM/EDXS (Hitachi S-4700 in the secondary electron mode, acceleration voltage 5-15 kV), and ICP-AES (Model 61E, Thermo Jarrell Ash, Woburn, MA). Platinum sputtering was used to make the coating surfaces conductive for the SEM investigations. In order to measure the thickness of the coat layers, the strips were tilted by 45 degrees and studied by SEM.

Bonding strength of coatings to the substrates was measured by using the method described in ASTM C-633 standard [11]. Both sides of the substrates were attached by using a drop of glue (with a tensile strength of 15 MPa) to cylindrical stainless steel jigs 10 mm in diameter and 15 mm in length. Tensile load was applied normally to the substrates with an Instron testing machine (Measurements Technology, Inc., Roswell, GA) at a crosshead speed of 1 mm/min until fracture occurred. The above sample preparation technique was previously utilized by Kokubo *et al.* [12] in testing the adhesion strength of bonelike apatite layers (about few microns-thick) obtained from SBFs of conventional recipes.

## RESULTS AND DISCUSSION

5 M KOH treatment applied to the strips was simply for the hydrothermal etching of the surfaces. Figures 1a and 1b showed the surface morphology and the XRD traces of those 5 M KOH + 600° C treated strips. The aggregated rosettes seen on the surface (Fig. 1a) belonged to a potassium titanate phase, possibly  $\text{K}_2\text{Ti}_2\text{O}_5$  [13], after the EDXS analyses. The surfaces of alkali-and heat-treated strips contained potassium titanate (peaks "1") and rutile,  $\text{TiO}_2$ , denoted by peaks "2." It should be noted that Yuan *et al.* [14] reported the formation of  $\text{K}_2\text{Ti}_{18}\text{O}_{17}$  nanowires, upon heating  $\text{TiO}_2$  powders in 8 M KOH solution, which would then decompose into  $\text{K}_2\text{Ti}_6\text{O}_{13}$  and  $\text{TiO}_2$  upon calcination at 600°C.  $\text{K}^+$  ions from the potassium titanate phase(s) on the surfaces of strips were released into the solution in exchange of  $\text{H}_3\text{O}^+$  ions, and resulted in the formation of a Ti-oxyhydroxide layer.  $\text{Ca}^{2+}$  ions coming from the coating solution reacted with this basic layer and formed there the nuclei of apatitic CaP globules.

The coating solution described above was not stable against precipitation (at RT) after the addition of  $\text{NaHCO}_3$  to raise its pH. The rise of pH in these solutions was quite monotonical (Fig. 2a). pH versus time curve depicted in Figure 2a was obtained after

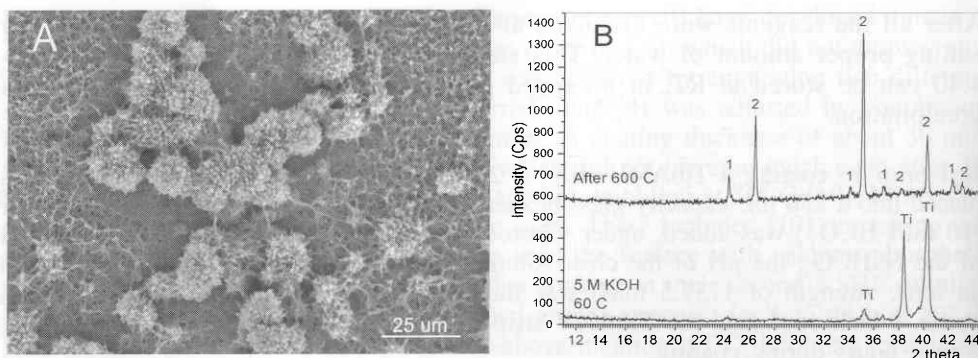


Fig. 1 - (a) SEM and (b) XRD data of 5 M KOH-soaked (60° C) and 600°C-treated Ti6Al4V strips

adding 1.68 g NaHCO<sub>3</sub> to 200 mL of solution given in Table I.

The stability against homogeneous precipitation only lasted from 5 to 10 minutes at RT, following the addition of NaHCO<sub>3</sub>.

After that period, solutions containing the metal strips slowly started to display turbidity (from 10 minutes to the end of the first hour), and by the end of 2 hours the solution turned opaque.

The colloidal precipitates formed in the solution stay suspended, and could only be separated from the mother liquor by centrifugal filtration (>3000 rpm). However, it is interesting to note that the solution pH at the end of 2 hours of soaking period stayed the same or slightly increased to around 6.57 or 6.58. That slight increase in pH was ascribed to the release of CO<sub>2</sub>. A pH decrease would have been encountered during the formation of colloidal precipitates due to H<sup>+</sup> release, but such a pH drop is not always observed [15]. To perform a run with 6 hours of total soaking time, the coating solution for the same strip was replenished twice with a new transparent solution (of pH = 6.5) at the end of each 2-hours segment. The start of precipitation indicated the stage where the solution reached supersaturation.

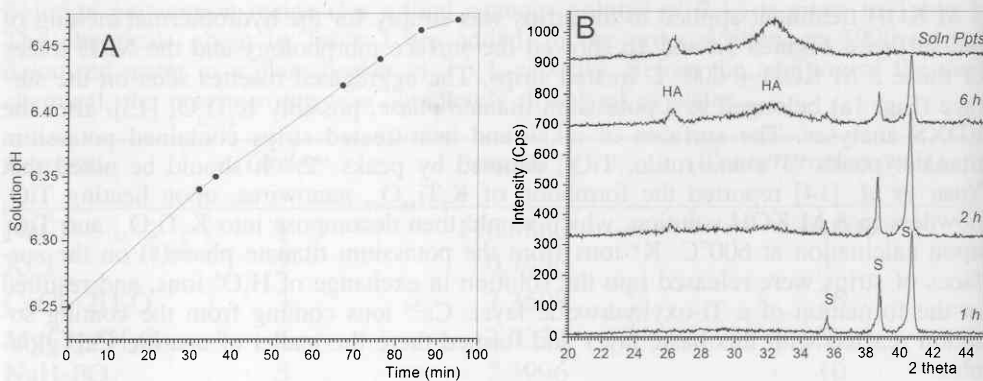


Fig. 2  
(a) pH change after NaHCO<sub>3</sub> addition, (b) XRD traces of uncoated and coated strips

The HCO<sub>3</sub><sup>-</sup> concentration employed and it was much lower than the "bubbling" method [10]. Increases in pH result in calcium phosphate-like coatings (30 wt% of carbonate ions [9]). Such a linear and enhanced coating thickness as a function of this new method. With the method for instance, the maximum coating thickness (i.e., 72 hours) of deposition f

Soak time (h)

- 1
- 2
- 4
- 6

Figure 3 depicts the SEM photographs of the surface of Ti6Al4V strips as a function of coating time (1 h, 2 h, 4 h, 6 h). By using 10 SBF solutions deposited on the surface of Ti6Al4V strips are shown in Figure 3a) with a smooth, nano-textured surface. At the end of the second hour in the SBF solution, however, the attachment of the coating on the smooth surface becomes more porous. The morphology of the hydroxyapatite were quite similar to those reported for SBF coating, excepting that big agglomerates were not met in our study. SEM micrographs for the purposes only. It was recorded in a buffered SBF of pH 7.4, with a soaking time of 6 weeks at 37° C.

A conventional SBF solution (pH 7.4) of apatitic calcium phosphate is reported here achieves this in only 6 hours. Figures 3c and 3d showed the formation of nanoclusters.

The significant extent of surface coating, was exemplified in Figure 3e.

The adhesion strength of the coating on the strips. Kokubo *et al.* [12] reported that the adhesion strength of apatite layers formed (by immersion) on titanium metals to range from

The  $\text{HCO}_3^-$  concentration employed in this robust coating process was only 10 mM, and it was much lower than those used in "5 SBF + continuous (for 72 hours)  $\text{CO}_2$ -bubbling" method [10]. Increased carbonate concentration in a coating solution would result in calcium phosphate-like solid deposits with unacceptably high levels (25 to 30 wt%) of carbonate ions [9]. Table 2 shows the deposition rate (measured in terms of coating thickness) as a function of immersion time.

Such a linear and enhanced coating rate has also been one of the advantageous sides of this new method. With the use of 5 SBF solutions under constant  $\text{CO}_2$  bubbling, for instance, the maximum coating thickness attained was around 35  $\mu\text{m}$  after 3 days (i.e., 72 hours) of deposition [10].

Soak time (h)	Coating thickness ( $\mu\text{m}$ )
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1	$13 \pm 2$
2	$22 \pm 2$
4	$46 \pm 4$
6	$68 \pm 5$

Table II - Coating thickness as a function of soaking time at RT in 10 SBF

Figure 3 depicts the SEM photomicrographs of coated surfaces of Ti6Al4V strips as a function of coating time (1 to 6 h; Figs. 3a through 3e) at RT.

By using 10 SBF solutions described here, the surface of the alkali- and heat-treated surface of Ti6Al4V strips are rapidly covered within the first hour of immersion (Fig. 3a) with a smooth, nano-textured calcium phosphate layer of about 13 nm-thick. By the end of the second hour in solution, coating develops to a thickness of about 22 nm, however, the attachment of calcium phosphate globules onto that initially-formed smooth surface becomes more enhanced (Fig. 3b). Such globules of apatitic calcium phosphate were quite similar to the previously reported results relevant to biomimetic SBF coating, excepting that biomimetic conditions (i.e., pH 7.4 and 37° C) were not met in our study. SEM micrograph given in Figure 3f is supplied for comparison purposes only. It was recorded from a Ti6Al4V strip soaked in *Tas*-SBF (a Tris-buffered SBF of pH 7.4, with a  $\text{HCO}_3^-$  concentration equal to 27 mM [8]) for 2 weeks at 37° C.

A conventional SBF solution (i.e., 1.5x*Tas*-SBF) can only coat a 20 nm-thick layer of apatitic calcium phosphate after two weeks of soaking at 37° C, while the 10 SBF reported here achieves this in only 2 hours at RT. High-magnification photomicrographs of Figures 3c and 3d showed that the globules actually consisted of petal-like nanoclusters.

The significant extent of surface coverage of the Ti6Al4V strip, in only 6 hours of coating, was exemplified in Figure 3e.

The adhesion strength of the coat layers was found to be  $12 \pm 2$  MPa, and there was virtually no difference in adhesion strength as compared to 1.5 X SBF-coated Ti6Al4V strips. Kokubo *et al.* [12] previously reported the adhesive strengths of "bonelike apatite layers formed (by immersion in conventional SBFs) on chemically treated titanium metals to range from 9.8 to 11.5 MPa." XRD data of the coated strips also

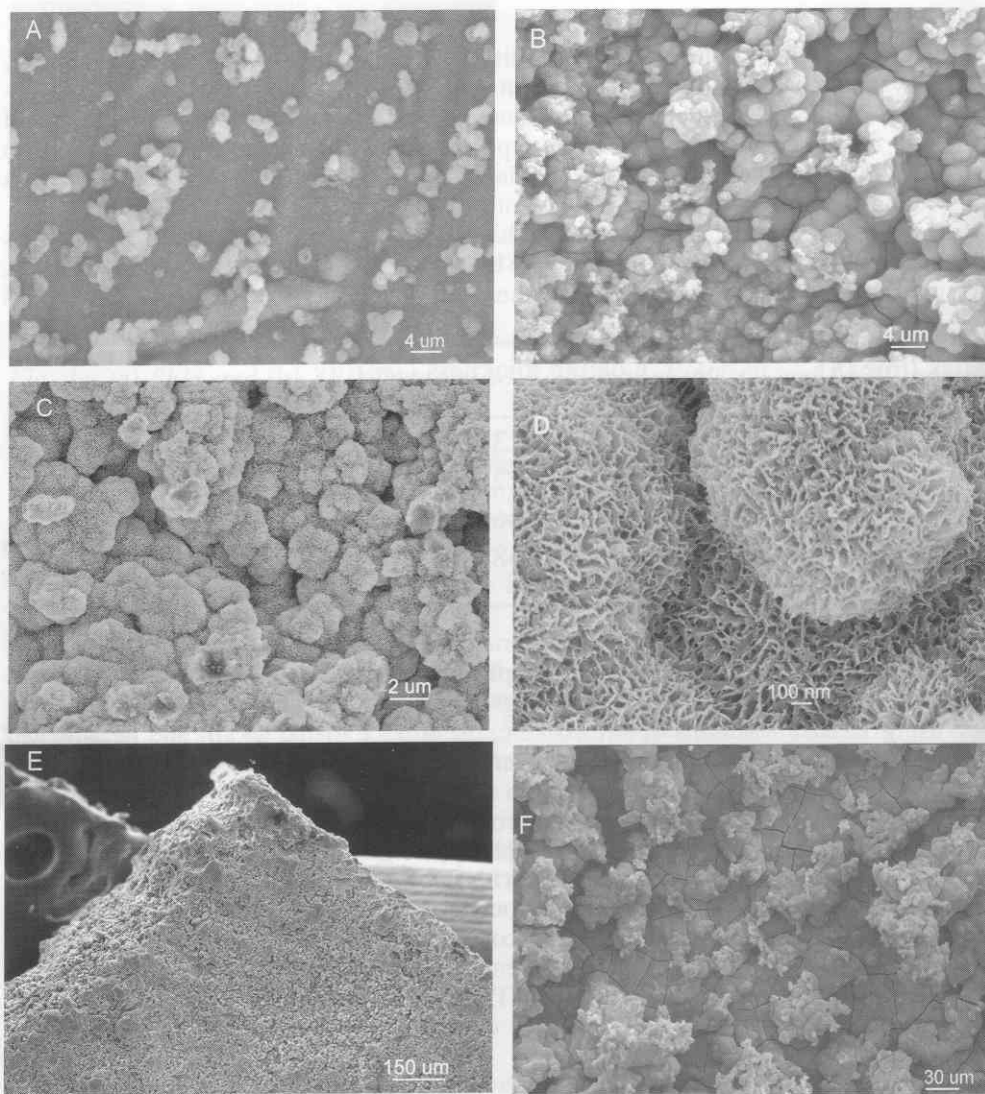
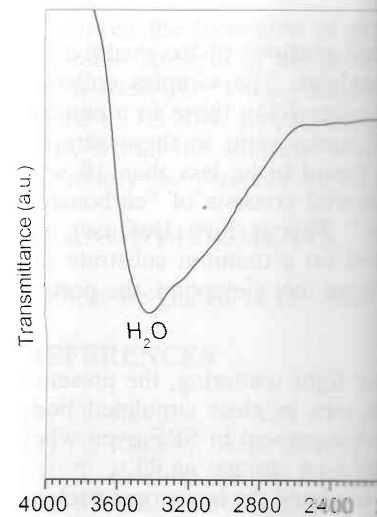


Fig. 3 SEM micrographs of CaP-coated Ti6Al4V strips in 10xSBF at RT; (a) 1 h, (b) 2 h, (c through e) 6 h, (f) Ti6Al4V strip soaked in 1.5SBF [8] for 2 weeks at 37°C

confirmed the apatitic nature of these globules, as shown in Figure 2b. Precipitates formed in the 10xSBF solutions were filtered from their mother liquor by centrifugation, washed three times with water, and once with ethanol, followed by drying at RT overnight. XRD data of these precipitates (Fig. 2b, top trace), as well as the FTIR data (Fig. 4), also indicated that the poorly-crystallized apatitic calcium phosphates did form in the solution. Bands of O-H stretching and bending of H<sub>2</sub>O were seen at, respectively, 3440 and 1649 cm<sup>-1</sup>. Presence of carbonate groups was confirmed by the bands at 1490-1420 and 875 cm<sup>-1</sup>. PO<sub>4</sub><sup>3-</sup> bands were recorded at 570 and 603 (n<sub>4</sub>), 962 (n<sub>1</sub>), 1045 and 1096 (n<sub>3</sub>) cm<sup>-1</sup> [8, 16].



If the sole aim of a process is to form a carbonated apatitic calcium phosphate coating, the value of a coating solution experiment has been successfully confirmed in the literature to be aware of the delicate balance between pH and temperature in determining the optimal set of those conditions [18]. Carbon dioxide (added for the sole purpose of forming a carbonate) simply retards the coating process, and to achieve a surface coverage one needs to

Fast coating solutions, sometimes called "one-step" are not new either; for instance, even in a TRIS-buffered SCS solution, calcium phosphate coat layers in *in vitro* [20] reported the room temperature coating of nickel-titanium alloy surfaces by calcium phosphate at the physiologic pH. The present work reports further improvements.

It is known that an amorphous calcium phosphate is formed during the precipitation of apatitic calcium phosphates in solution, such as the one used in the present work. The process of ACP formation in solution is a two-step process which then aggregated randomly (as seen in Figs. 2d and 4), with the ACP acting as precursors to the formation of calcium-deficient hydroxyapatite, the process converging to 1 [23].

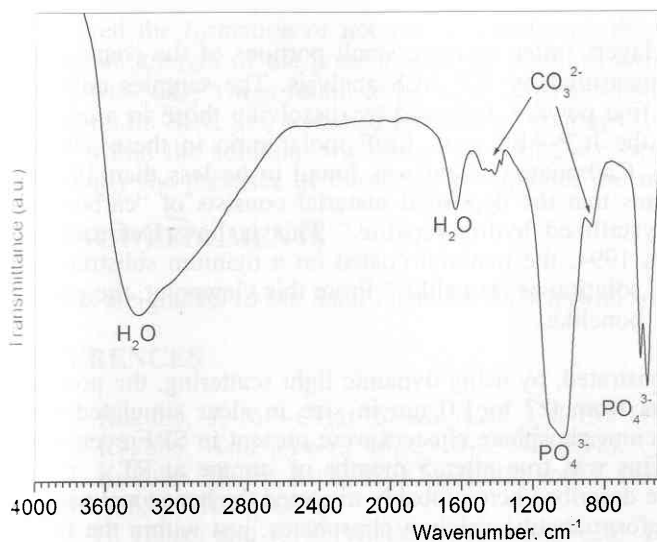


Fig. 4 FTIR data for calcium phosphates formed in 10xSBF solutions at RT

If the sole aim of a process is to coat titanium or titanium alloy surfaces with a carbonated apatitic calcium phosphate layer, then there is no need to maintain the pH value of a coating solution exactly at the physiologic value of 7.4. This point has been successfully confirmed in the work of Barrere *et al.* [10, 17]. One only needs to be aware of the delicate balance between the solution pH,  $\text{HCO}_3^-$  ion concentration and temperature in determining which phases will be soluble or not under a specific set of those conditions [18]. On the other hand, the presence of TRIS or HEPES (added for the sole purpose of fixing the solution pH at around 7.4) in a SBF formulation simply retards the coating process to the level that in order to obtain a decent surface coverage one needs to wait for 2 or 3 weeks [1-3].

Fast coating solutions, sometimes named as supersaturated calcification solutions (SCS) are not new either; for instance, the pioneering work of Wen *et al.* [19] showed that even in a TRIS-buffered SCS solution it would be possible to form 16 mm-thick calcium phosphate coat layers in after 16 hours of immersion. More recently, Choi *et al.* [20] reported the room temperature coating (about 10 mm-thick in 24 hours) of nickel-titanium alloy surfaces by a simple SCS solution, which was not even buffered at the physiologic pH. The present paper corroborates these previous findings and reports further improvements.

It is known that an amorphous calcium phosphate (ACP) precursor is always present during the precipitation of apatitic calcium phosphates from the highly supersaturated solutions, such as the one used here [21]. Posner, *et al.* [22] proposed that the process of ACP formation in solution involved the formation first of  $\text{Ca}_9(\text{PO}_4)_6$  clusters which then aggregated randomly to produce the larger spherical particles or globules (as seen in Figs. 2d and 4), with the intercluster space filled with water. Such clusters (with a diameter of about 9.5 Angstrom [21]) are probably the transient solution precursors to the formation of carbonated globules with the stoichiometry of a calcium-deficient hydroxyapatite, namely,  $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ , where  $x$  might be converging to 1 [23].

Ca/P molar ratio of the coat layers (after scraping small portions of the coatings off of the Ti6Al4V strips) was measured by ICP-AES analysis. The samples collected were carefully ground into a fine powder, followed by dissolving those in a concentrated acid solution prior to the ICP-AES runs. Ca/P molar ratio in these samples turned out to be  $1.57 \pm 0.05$ . Carbonate content was found to be less than 10 wt% (i. e.,  $8.2 \pm 0.3\%$ ). This means that the deposited material consists of "carbonated, calcium-deficient, poorly crystallized hydroxyapatite." This is how DeGroot and Kokubo [24] defined, back in 1994, the material coated on a titanium substrate immersed in a conventional SBF solution as "bonelike." From this viewpoint, the present coatings can be classified as bonelike.

Onuma *et al.* [25] have demonstrated, by using dynamic light scattering, the presence of calcium phosphate clusters from 0.7 to 1.0 nm in size in clear simulated body fluids. They reported that calcium phosphate clusters were present in SBF even when there was no precipitation. This was true after 5 months of storage at RT. The solution coating procedure described here probably triggered the hexagonal packing [25] of those nanoclusters to form apatitic calcium phosphates, just within the first 5 to 10 minutes, following the introduction of  $\text{NaHCO}_3$  to an otherwise acidic calcium phosphate solution. Since these nanoclusters are always present even in a conventional ionic strength SBF, the insertion of a suitable alkali- and heat-treated Ti6Al4V surface into such a solution immediately starts the coating process, as explained above. This is how the dense-looking under coat layer is formed (Figs. 3a, 3b, and 3f) in less than an hour, provided that the solution is concentrated and supplying enough Ca and  $\text{HPO}_4^-$  ions to the metal-solution interface.

What is achieved here, with this new solution [26] in less than an hour, can only be done with a conventional SBF in about a week. On the other hand, the colloidal precipitates (as a result of the hexagonal packing of the invisible nanoclusters [25]) of 10xSBF solution are formed by a homogeneous nucleation process. The presence of these precipitates within the solution, possibly, further accelerates the coarsening of the newly deposited calcium phosphate globules. Conventional, Tris or Hepes-buffered SBF solutions (1.5 SBF) are able to form those precipitates by the end of 2<sup>nd</sup> or 3<sup>rd</sup> day of soaking at 37° C. Since the Ca/P molar ratio of all SBF solutions (including the one presented here) are 2.50, they are not stable against hydroxyapatite precipitation when the solution pH is higher than 6.4 [8, 9].

## CONCLUSIONS

The use of  $\text{NaHCO}_3$  with a concentrated (10 times of  $\text{Ca}^{2+}$  and  $\text{HPO}_4^{2-}$  ion concentrations) simulated body fluid-like solution of ionic strength of 1137.5 mM allowed the formation of a bonelike apatitic calcium phosphate layer on Ti6Al4V at room temperature within 2 to 6 hours. The coating solutions of pH 6.5 did not necessitate the use of buffering agents.

The pH adjustment was achieved by a single addition of  $\text{NaHCO}_3$ . The coating process did not necessitate the continuous bubbling of  $\text{CO}_2$  during the process. This robust process had a linear and fast coating kinetics. The surfaces of the Ti6Al4V strips were chemically etched in 5 M KOH solution and thermally treated afterwards at 600°C, prior to soaking in 10 x SBF. KOH soaking and thermal treatment following

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it ensured the formation of potassium titanates on the strip surfaces. Adhesion strength of the present bonelike coatings (with a Ca/P molar ratio of 1.57 and 8 wt% CO<sub>3</sub><sup>2-</sup>) was found to be 12 ± 2 MPa, which was comparable to that obtained in 1.5 SBF, i.e., so-called biomimetic coatings. Formation of colloidal precipitates, within the solution, was observed during the first hour of soaking at RT, but apparently the presence of those fine precipitates did not hinder the coating process.

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