

# 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, until 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 solution was then placed into a 250 mL-capacity glass bottle, which contained the Ti6Al4V strips, and the strips were immersed for 2 to 6 hours during coating.

Samples were characterized by XPS, operated with Cu K<sub>α</sub> radiation at 10 kV, Nicolet 550, Thermo-Nicolet. For secondary electron mode, accelerated voltage was 10 kV, Thermo Jarrell Ash, Woburn, MA. For SEM, surfaces were coated with Au for conductivity. For the SEM, the coat layers, the strips were tested. Bonding strength of coatings to substrates was tested as described in ASTM C-633 standard. For XPS, by using a drop of glue (with a steel jigs 10 mm in diameter and attached to the substrates with an Instron 1130, Roswell, GA) at a crosshead speed of 0.5 mm/min. The sample preparation technique was the same as the adhesion strength of bonelike coatings from SBFs of conventional recipes.

## RESULTS AND DISCUSSION

5 M KOH treatment applied to the Ti6Al4V surfaces. Figures 1a and 1b show the surfaces of those 5 M KOH + 600° C treated strips. The surface (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 solution reacted with this basic layer to form a phosphate layer.

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

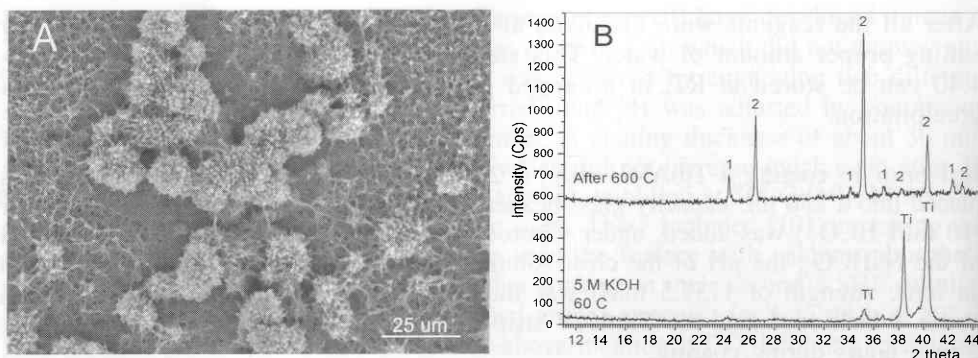


Fig. 1 - (a) SEM and (b) XRD data of 5 M KOH-soaked (60° C) and 600°C-treated Ti6Al4V strips

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.

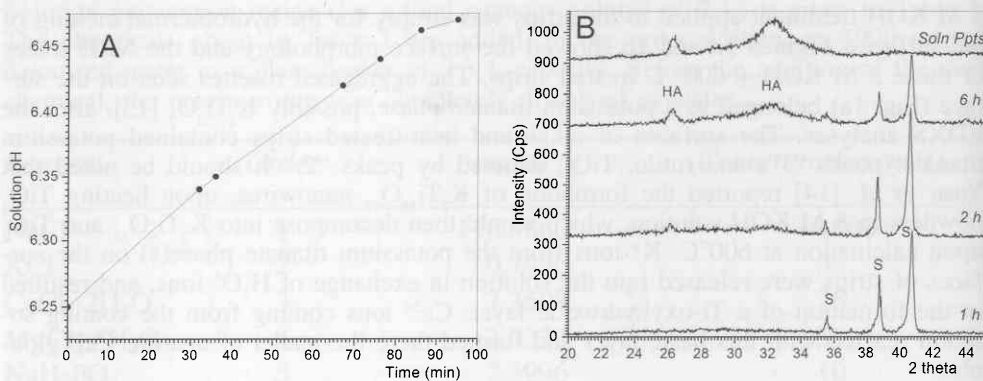


Fig. 2  
(a) pH change after NaHCO<sub>3</sub> addition, (b) XRD traces of uncoated and coated strips

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 calcium phosphate were quite similar to those reported for SBF coating, excepting that big clusters 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 one week. 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  $\mu\text{m}$ -thick. By the end of the second hour in solution, coating develops to a thickness of about 22  $\mu\text{m}$ , 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  $\mu\text{m}$ -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