JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **11** (2000) 787–792

Dissolution behavior of plasma-sprayed hydroxyapatite coatings

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The long-term stability of plasma-sprayed hydroxyapatite coatings is influenced by the dissolution behavior of the coating in *in vivo* conditions. Plasma-spraying generates a mixture of phases and this study has focused on how the balance of phases affects the *in vitro* dissolution behavior of the coatings in double distilled-deionized water and in tris-buffer solutions. The pH changes in double distilled-deionized water were monitored, whilst the pH value was maintained at 7.25 for the tris-buffer solution at 37 °C with 5% CO_2 atmosphere. The phosphate and calcium ions released were measured using UV-Visible Spectrophotometer and Atomic Absorption Spectroscopy respectively. Changes in crystal and surface topology were also studied. The results indicate that the dissolution behavior of the coatings depends on several factors. The rate of release of phosphate ions was found to increase significantly for the tris-buffer solution compared to the deionized water, indicating that the presence of electrolyte constituents affects the dissolution behavior of the coatings. The Ca/P ratio in the tris-buffer solution is approximately three. Increases in the level of crystallinity of the coatings significantly decreased the dissolution rate and hence, the amount of phosphate ions released. The higher the percentage of crystallinity, the higher the stability of the coating under *in vitro* conditions.

1. Introduction

Hydroxyapatite (HA) coatings on metallic implants, such as titanium, have found widespread clinical applications. However, there has lately been a growing conflict as to whether these coatings should deliver long-term stability or need to only function temporarily to be effective in promoting a good tissue interface.

Those in favor of long-term stability reason that the coating is important due to the clinical improvements in the quality of the tissue interface which are clearly caused by the presence of coatings as compared to the uncoated implants [1–5]. On the other hand, there are those who believe that since the HA coating promotes a rapid integration of implant to bone, the actual presence of the coating is not essential once satisfactory integration has been established [6–8].

To deliver better *in vivo* stability, for long-term performance, HA coatings should be highly crystalline, thus achieving a lower biodegradation rate as compared to amorphous or partly amorphous coatings [9]. However, bone apposition was reported to be related to the dissolution behavior of the coatings, requiring the presence of amorphous or partly amorphous component [10]. Therefore a coating is expected to possess long-term stability and at the same time acts as a reservoir of calcium and phosphate ions for inducing greater bone formation and bone bonding.

Plasma-spraying is the most common commercial technique of producing HA coatings. The very high temperature of plasma-spraying, usually beyond the melting temperature of HA, 1550 °C [11–12], will unavoidably change the calcium phosphate phases and crystallinity through thermal decomposition. It is well known that the plasma-spraying generates a mixture of phases such as crystalline stoichiometric hydroxyapatite (sHA), calcium-deficient hydroxyapatite (CDHA), oxy-hydroxyapatite (OHA), calcium oxide CaO, α- and β-tricalcium phosphate (TCP) and tetracalcium phosphate (TeCP) [12–15]. Variations in plasma-spraying parameters can therefore lead to profound effects on the dissolution behavior of the coatings.

It was reported that the comparative dissolution behavior of different monophasic calcium phosphates in increasing order is as shown below [16]:

$$\text{sHA} < \text{CDHA} < \text{OHA} < \beta\text{-TCP} < \alpha\text{-TCP} < \text{TeCP}$$

Since the dissolution behavior of the coatings reflects their phases distribution, the presence of metastable components (e.g. TCP, TeCP) in turn leads to an increase in instability of the coatings. Therefore the phase balance of the plasma-sprayed coating may affect its long-term behavior in *in vivo* conditions.

Other factors that may affect the dissolution behavior of the coatings are porosity, surface morphology such as cracks, loading conditions, duration of immersion, pH, buffer capacity, electrolyte constituents and the presence of proteins and cells [13, 16–18].

In this study plasma-sprayed HA coatings were produced using commercial HA powder, and tested under different *in vitro* conditions by means of immersion tests. The aim of the study was to investigate the dissolution behavior of the coatings immersed under deionized water and tris-buffer solutions. The changes in pH and the effects of crystallinity on the dissolution behavior were also monitored.

2. Materials and methods

HA powder (Captal 60) supplied by Plasma Biotal Ltd, UK, was used. The powder was plasma-sprayed using an F4 Gun All-Gas System (Plasma Technik Ltd, UK), following the parameters as shown in Table I. It was plasma-sprayed onto pure titanium discs (Titanium International Ltd, UK), of 14.0 mm diameter × 1.0 mm thickness, until coating thicknesses of between 100–125 microns were achieved. The HA-coated discs were then immersed in double distilled-deionized water and calcium- and phosphate-free tris-buffer solution at 50 ml volume each in an oven at temperature 37 °C with 5% CO_2 atmosphere.

Tris-buffer solution was prepared by dissolving 50 mM tris-hydroxymethyl-aminomethane [$(CH_2OH)_3CNH_2$; MW = 120.10] supplied by Sigma Aldrich Co. Ltd, in double distilled-deionized water. It was then stabilized at pH 7.25 with HCl at body temperature 37 °C. The evaluation of dissolution behavior was made by measuring the concentrations of phosphate and calcium ions released into the solutions at 24 h intervals for 336 h using UV-Visible Spectrophotometer (CECIL, CE 2303) and Atomic Adsorption Spectroscopy (Perkin-Elmer Model 370) respectively. From these results, Ca/P ratio in the immersion solution can be calculated.

The changes in crystal structure were monitored using a Philips X-Ray Diffractometer (XRD), and surface morphology was examined using a Scanning Electron Microscope (SEM, JEOL JSM 5300LV, UK). To obtain the exact surface location for SEM studies, a masking technique was used. A mask of the same dimension as the disk with a tiny hole in the center covered the surface of the disk. Therefore the area of the hole which represents the exact center of the coating was evaluated before and after immersion tests. The use of the JEOL 5300LV SEM allowed the surface to be examined without coating, allowing sequential observation during dissolution.

TABLE I Plasma-spraying parameters

Parameters	Standard settings
Injector nozzle diameter (mm)	1.5
Injector distance (mm)	6
Injector angle (degrees)	90
Plasma-spraying distance (mm)	75
Speed of rotation of substrate surface (m/s)	15.5–19.0
Speed of torch movement (m/s)	–
Current (Amp)	450
Voltage (V)	57 ±
Primary gas	Argon
Flow rate (1/min)	15.5
Secondary gas	Nitrogen
Flow rate (1/min)	12
Carrier gas	Argon
Flow rate (1/min)	4.5

In order to change the coating crystallinity and to investigate its effects on the immersion behavior, the HA-coated disks were heat-treated in atmospheric conditions at a temperature of 600 °C for 1 h before undergoing similar immersion tests.

3. Results

3.1. Characterization of HA coatings

The plasma-sprayed HA coatings produced in this study were white-gray in color. The coatings were found to contain many pores and micro-cracks as shown in Fig. 1. The XRD spectrum in Fig. 2(a) reveals the coating composition and structure as compared to Fig. 2(b) of pure control HA powder, which is 100% crystalline. The XRD peaks, which sit on a broad background peak, indicate that the coating is now a combination of crystalline and amorphous phases as a result of thermal decomposition from the plasma-spraying process. The peaks that were characteristic of HA can still be seen clearly but have reduced in intensity to varying degrees. Besides HA, the coating now distinctly contains other phases such as calcium phosphate hydrate ($d = 3.033$, $2\theta = 29.455°$) and calcium oxide phosphate ($d = 2.077$, $2\theta = 43.539°$). Traces of minor peaks also indicate the presence of tricalcium phosphate ($d = 2.88$, $2\theta = 31.027°$).

3.2. Immersion results

In order to study the general dissolution behavior of the coating, immersion tests under double distilled-deionized water were first carried out. Fig. 3 shows the changes in the dissolution behavior, by means of phosphate ions released into the solution, and the pH values with respect to time. It was found that the concentration of phosphate ions increases until it reaches an equilibrium condition. Whereas the pH value drops

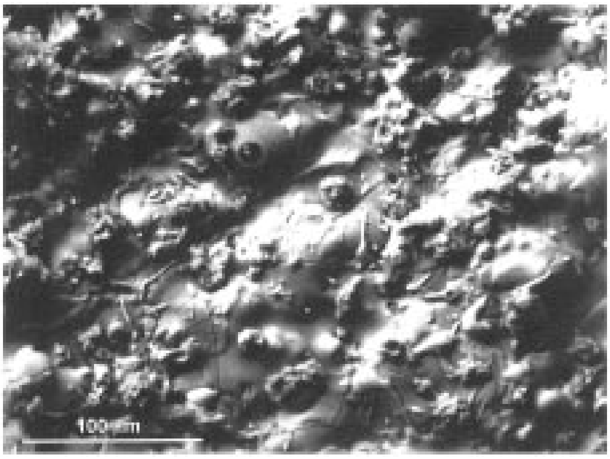

Figure 1 Surface morphology of plasma-sprayed HA coating (SEM).

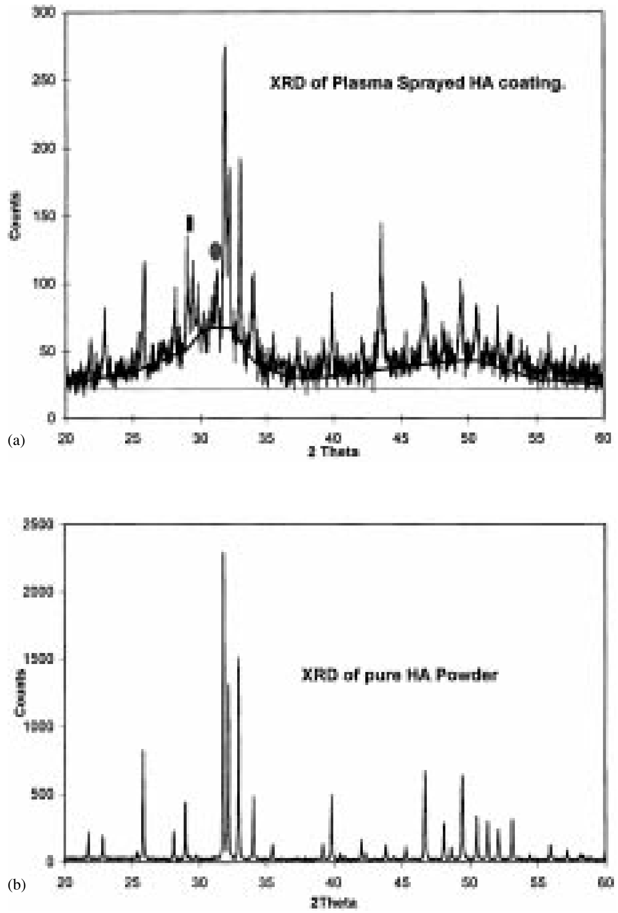

Figure 2 X-ray diffraction patterns (40 kV, 30 mA, scanning rate 0.02°/s, CuK_α radiation) of (a) plasma-sprayed HA coating with ▮ of calcium phosphate hydrate and ● of tricalcium phosphate peaks and (b) pure HA starting powder.

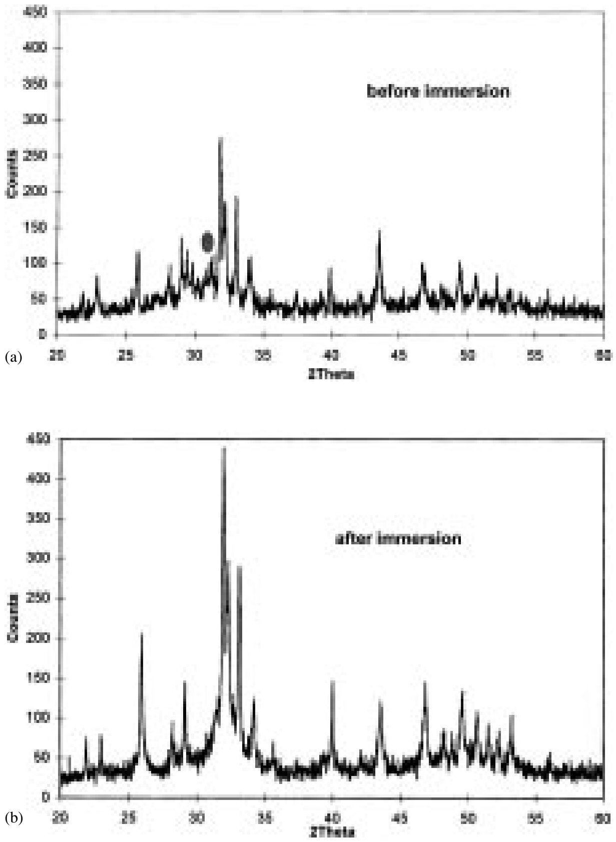

Figure 4 X-ray diffraction patterns of HA coating (a) before and (b) after immersion in double distilled-deionized water, with ● of tricalcium phosphate peak.

initially from 7.54 to about 6.02 before stabilizing at a pH of about 6.3.

Fig. 4(a) and (b) show the X-ray diffraction patterns of the coating before and after immersion, respectively. The peaks were more defined indicating that there is a slight increase in crystallinity, even though the broad amorphous phase peak seems to remain unaltered. Minor peaks, such as at d-spacing = 2.860 ($2\theta = 31.027°$), which indicate the presence of metastable TCP component were found to have disappeared after immersion. This result seems to confirm that the reaction of TCP, is the reason for the increase in phosphate ions detected. This dissolution behavior can clearly be seen by the SEM microstructures of before and after immersion, of the exact same surface location as shown in Fig. 5(a) and (b) respectively. The surface now contains more microcracks.

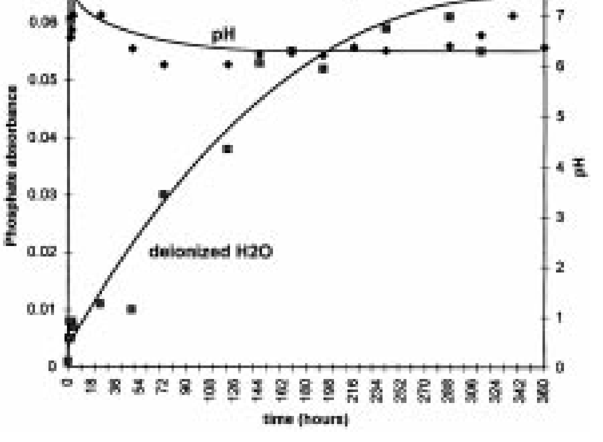

Figure 3 Phosphate absorbance and pH changes with respect to time of HA coatings immersed in double distilled-deionized water.

Immersion tests undertaken under calcium- and phosphate-free tris-buffer solution seem to undergo a similar reaction trend as in double distilled-deionized water, except that the dissolution process was more rapid and greater in magnitude. This is shown in Fig. 6. The dissolution rate increases with time until it reaches an equilibrium condition. The amount of phosphate ion released into the tris-buffer solution was almost double that released in the deionized water.

Fig. 7 shows the concentrations of calcium and phosphate ions released into the tris-buffer solution over time. It was found that the release of calcium ions was much higher than that of phosphate ions. The Ca/P ratio at any one time in the tris-buffer solution is approximately three.

To investigate the behavior of the coating under different levels of crystallinity, the coatings were fired at 600 °C for 1 h under atmospheric condition. The white-gray color of the coatings turns green after firing, indicating pure hydroxyapatite structure with lattice defects. This is further demonstrated by the XRD spectra as shown in Fig. 8(a) and Fig. (b) from before and after

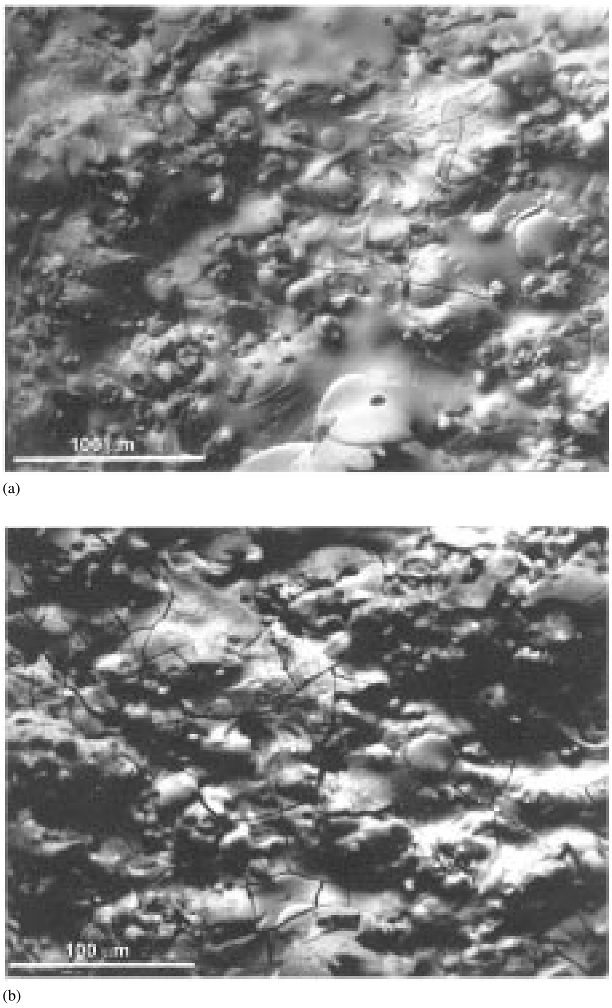

Figure 5 Exact surface morphology of plasma-sprayed HA coating of (a) before and (b) after immersion in double distilled-deionized water.

firing, respectively. Only the peaks that are characteristic of hydroxyapatite were seen after the firing process. Immersion tests of fired coatings done under tris-buffer solution do not show any significant dissolution behavior as compared to the untreated coatings, as shown in Fig. 9.

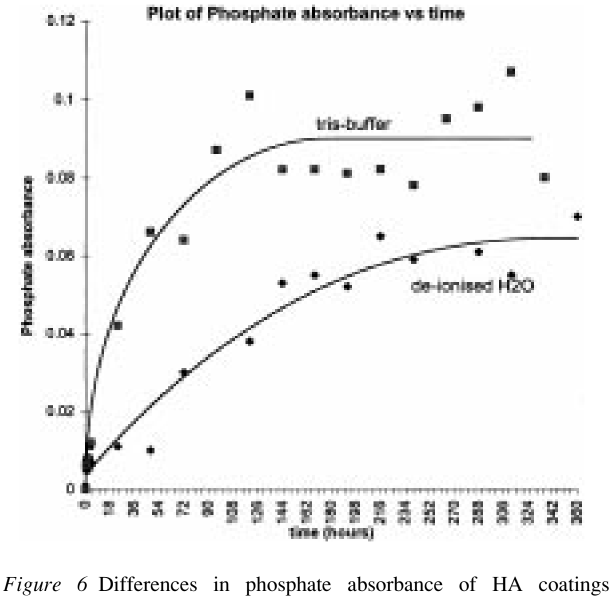

Figure 6 Differences in phosphate absorbance of HA coatings immersed in tris-buffer solution and double distilled-deionized water with respect to time.

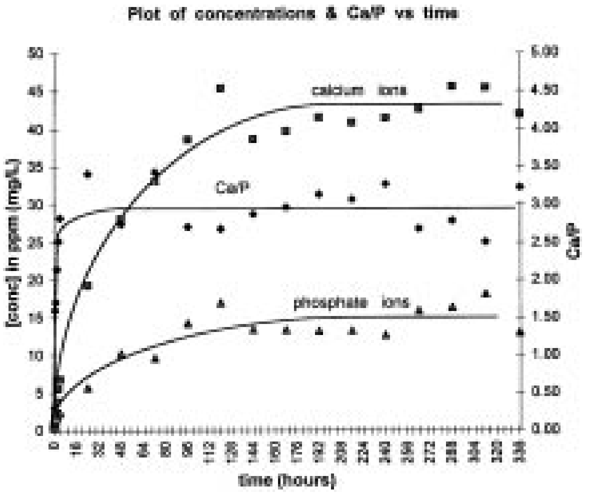

Figure 7 Concentrations of calcium and phosphate ions released into tris-buffer solution with respect to time and the corresponding Ca/P ratio.

4. Discussion

These studies set out to examine the dissolution behavior of plasma-sprayed HA coatings under two immersion solutions and at an increased level of crystallinity. The data obtained clearly demonstrate that the dissolution behavior of the coatings can vary significantly depending on the percentage of crystallinity and the presence of electrolyte constituents in the test solutions.

Double distilled-deionized water tests were undertaken to facilitate the study of the general dissolution behavior of the coatings. Since the ion concentration in water is not in equilibrium with that in the coatings, it not

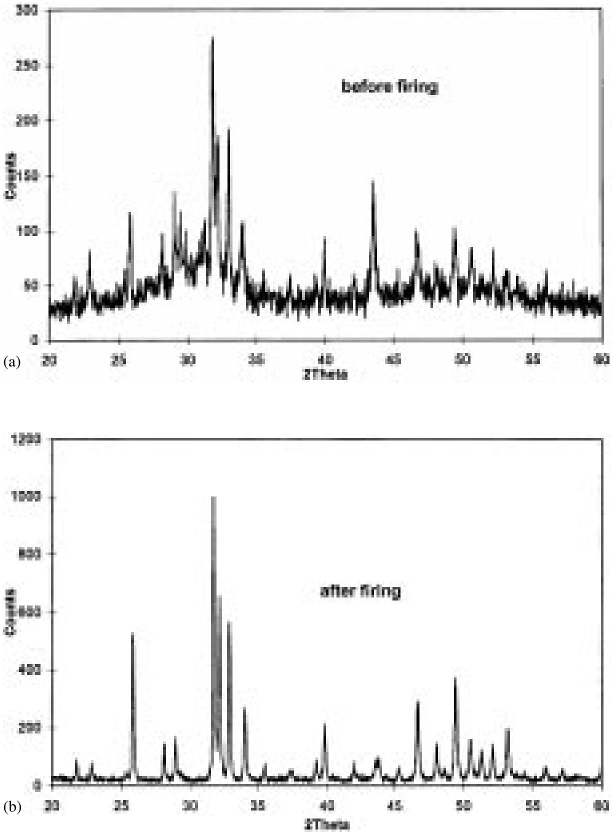

Figure 8 X-ray diffraction patterns of HA coating (a) before and (b) after firing at 600 °C for 1 h in atmospheric condition.

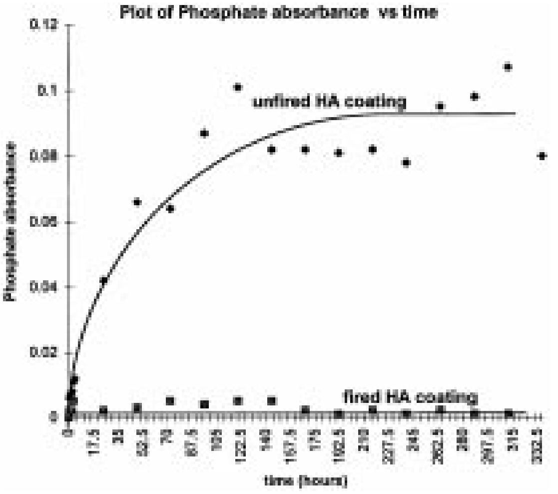

Figure 9 Differences in phosphate absorbance of fired and unfired HA coatings immersed in tris-buffer solutions with respect to time.

only induces dissolution reactions until ionic saturation is achieved at an equilibrium point, but also affects the pH value of the system [19]. The released ions, in the forms of Ca^{2+}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and $CaH_2PO_4^+$ [20], increase the concentrations of calcium and phosphate ions in the solution. Since the system is not buffered, the presence of weak phosphoric acids (e.g. $H_2PO_4^-$, HPO_4^{2-}) due to the initial dissolution behavior reduces the pH value as shown in Fig. 3.

The surface chemistry of an HA coating is greatly affected by the balance of phases and the pH in its microenvironment. Since the dissolution of the metastable components obviously occurs at the initial stage of immersion tests, similar reactions could be expected when the coating is implanted in *in vivo* condition, especially when a decrease in pH value occurs due to infection and inflammation. Acidification of the microenvironment could also occur due to cellular interaction [21]. However, large pH changes are unlikely to occur around an implant *in vivo* as blood, which is extremely well buffered, is present in large volume and constantly circulating.

Phases such as TCP react with water molecules to form a crystalline apatitic structure by inclusion of defects according to the reaction [22]:

$$4Ca_3(PO_4)_2 + H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 2Ca^{2+} + 2HPO_4^{2-} \qquad (1)$$

Hence leading to a slight increase in crystallinity as can be seen in Fig. 4(b). This is also in agreement with the observation made by de Groot *et al.* [23], when coatings were kept in aqueous solutions for several weeks, who found that the coatings crystallinity increases.

The top surface layer of the coating was found to have dissolved during immersion, while more micro-cracks seemed to have appeared as shown in Fig. 5(b). The dissolved layer may expose micro-cracks already present within the coatings or may also propagate existing surface cracks due to internal (residual) stresses being released [18].

The effects of electrolyte constituents at a constant physiologic pH 7.25 were also studied using tris-buffer solution. Tris-buffer [$(CH_2OH)_3CNH_2$], which contains three active hydroxyl ion groups and is stabilized by HCl, may react with the calcium ions released from the coatings. Hence, creating an active environment to induce more dissolution to occur, especially for the calcium ions, until it reaches an equilibrium stage as compared to the immersion in deionized water. Similarly, Reis *et al.* [17] in their study of the effects of Hank's Balance Salt solution (HBSS) on the dissolution behavior of the HA coatings, concluded that the more complex the test solution is, the more aggressive it is in reducing the coatings stability.

Firing the coatings at 600 °C for 1 h increases the percentage of crystallinity of the coatings to almost 100%. The heat treatment enables the coatings to react with moisture in air and to incorporate hydroxyl ions into the amorphous structure. The increase in crystallinity renders the coatings effectively ''insoluble'' within the time frame of the experiment as shown in Fig. 9. However, since the percentage of the amorphous phase is almost negligible, ''site'' dissolution may have occurred but was too small to be detected.

These experiments were undertaken in static fluid conditions, and therefore local build-up of solutes may have occurred. The test solution was not replenished with fresh solution for the duration of the experiment and the solution's initial composition was not maintained. This approach was adopted to avoid introducing other variables into the experiments. However, dissolution *in vivo* does not occur in a constant volume of fluid. This is because once dissolved, the ions can be transported away from the dissolution sites by fluid flow. Therefore equilibrium condition may never be reached. However, these studies may indicate the effects of electrolyte constituents and the coating's crystallinity in the initial implant behavior in *in vivo* conditions. In addition the ionic binding and linking ions to the surface of the HA may create a stagnant layer adjacent to the surface which is more static in characters.

5. Conclusions

Dissolution studies undertaken in double distilled-deionized water demonstrate that the metastable components of the plasma-sprayed coatings dissolved under aqueous solution and hence increased the phosphate ions in the solution. The presence of electrolyte constituents in the test solution, such as calcium- and phosphate-free tris-buffer solution, will also increase the rate of dissolution further as compared to the deionized water. Increases in the coating crystallinity, however, will decrease the rate of dissolution. The pH value also plays an important role in the coating dissolution behavior. The dissolved components of the coatings generated weak phosphoric acids, which increase the dissolution reaction of the coatings in microenvironment.

Acknowledgments

The authors are grateful for the financial support from SIRIM Berhad Malaysia towards this research.

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Received 4 August 1998
and accepted 22 July 1999