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Cladding of Titanium/Fluorapatite composites onto Ti6Al4V substrate and
the *in vitro* behaviour in the simulated body fluid

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Abstract

To improve the bioactivity of Ti6Al4V alloy, an innovative cladding method has been developed to bond a Ti/fluorapatite (FA) composite onto the alloy for load-bearing applications. With the aid of a silver interlayer and external pressure during sintering, a defect-free interface between the composite and the substrate was obtained. The fabricated materials were bioactive and could induce the nucleation and formation of bone-like carbonated apatite after immersed in the simulated body fluid (SBF). Functional ions, such as Ag^+ and F^- , were released from the materials during immersion, which could impart favourable activities for the implant. This work demonstrated that a simple and novel method could be applied to enhance functionalities of Ti alloys for load-bearing implant applications.

Keywords: titanium; fluorapatite; cladding; simulated body fluid

1 Introduction

Fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FA), in which the fluorine substitutes the entire hydroxyl group in hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA), is regarded as a promising biomaterial for bone and tooth implant due to its similarities to HA with additional benefit of fluorine release [1, 2]. Early studies in dental applications of FA have revealed that fluorine is able to retard the acidic attack of caries by being incorporated into the dental enamel to form a fluorapatite surface [3-5]. Later on, the physiological significance of fluorine ions in promoting mineralization and crystallization of calcium phosphate in bone forming was established [6-9]. It has demonstrated that Ti/HA composites fabricated by powder

metallurgy are biocompatible and bioactive both *in vitro* and *in vivo* [10-14]. Due to the similarities between FA and HA in both physical and chemical properties, it is expected that Ti/FA composites will also be biocompatible and bioactive, with potentially additional benefit of fluorine release.

On the other hand, Ti6Al4V is one of the most popular Ti alloys used as load-bearing implants due to its good biocompatibility, excellent corrosion resistance and superior mechanical properties [15, 16]. However, Ti6Al4V is a bioinert material which cannot induce biological fixation to the surrounding tissues after implantation [17]. To improve the bioactivity of the alloy and enhance the implant-tissue osseointegration, calcium phosphate (Ca-P) surface coating is commonly used in various medical implant applications [18]. Because of the substantial differences in the chemical and physical properties between the coating and the substrate, many defects, such as cracks and voids, would present in the interface, resulting in an early degradation and failure of the surgery [19].

Silver has been successfully used as an interlayer to aid the joining of dissimilar materials by diffusion bonding [20, 21]. In addition, silver is also known to provide broad-spectrum antimicrobial property, which is particularly significant for the polymicrobial colonization associated with biomaterial related infections [22, 23]. In the body fluid environment, silver can release ions to damage bacterial RNA and DNA, thus inhibiting their replications [24]. Both metallic and ionic silver have been incorporated into biomaterials such as polyurethane, hydroxyapatite and bioglasses [22, 25-27].

To explore the benefits of fluorine and silver for enhanced biological functions and improve bonding strength in load-bearing implant applications, Ti/FA composites was

bonded onto Ti6Al4V substrate with the assistance of a silver interlayer. The interface and surface of the fabricated material were characterized and the bioactivity of the material was evaluated in the simulated body fluid (SBF) environment.

2 Experimental procedures

2.1 Preparation of the composites

The FA powder was synthesised according to the following solid reaction between calcium phosphate and calcium fluoride [28]:

$Ca_3(PO_4)_2$ and CaF_2 (Sigma-Aldrich, Germany) in stiochoimetric molar ratio were mixed with ZrO_2 balls in ethanol for 48 hrs by a 3D mixer (Laval Lab, Canada). After drying, the mixture was compacted into cylinders and heat-treated in argon at 1200 °C for 4 hrs. The obtained solid FA cylinders were subsequently ground into powders and then screened with a 325 mesh sieve. 5 and 10 vol.% of FA powders were mixed with commercially pure Ti powders (Atlantic Equipment Engineers, USA) in an argon atmosphere for 48 hrs.

Ti6Al4V samples with dimensions of 8 mm × 8 mm × 1.7 mm were cut from a 1.7mm thick plate (RMI Titanium Company, Mississauga, Canada). After one surface was polished to mirror-like finish, the samples were ultrasonically cleaned in acetone, ethanol and deionised water, followed by drying in air. A single layer of 25 µm thick silver foil (Alfar Aesar, USA) was then placed on the polished surface, and the sample was put inside of a rigid tool-steel die. 1 gram of the Ti/FA mixture was then uniformly distributed on the top of the silver foil and a uniaxial pressure of 350 MPa was applied to

compact the mixture onto the Ti6Al4V substrate. The compacted sample was sintered in argon atmosphere at 1100 °C for 1 hr under a 0.1 MPa external pressure. For convenience, the sample with X volume percent of FA was denoted as TXFAT. For comparison, Ti/FA composite was also bonded to the Ti6Al4V substrate without external pressure or the silver interlayer under the same heating scheme.

2.2 *In vitro* test in the simulated body fluid (SBF)

To evaluate the *in vitro* behaviour of the bonded material, an SBF solution was prepared according to the recipe described by Kokubo et al. [29]. Because the SBF can be easily contaminated by bacteria in ambient environment, 1g/l NaN₃ was added to the solution to inhibit the growth of the anaerobic bacteria and maintain the ion concentrations in the solution [30]. The ion concentrations in the SBF and human blood plasma were listed in Table 1.

Table 1 *Inorganic ion concentrations in the simulated body fluid (SBF) and human blood plasma (mM)*

The as-sintered composite samples were polished with sandpaper up to 1200 grit and then washed ultrasonically in acetone, ethanol and deionised water for 10 minutes each, followed by drying with a heat gun. The samples were soaked in the SBF for various periods, and then removed from the SBF, gently rinsed with deionised water and dried naturally in a fume hood.

2.3 Characterizations

The phases in the sintered samples were characterized by X-ray diffraction (XRD, X'Pert, Philip, Netherlands), with Cu K α radiation at 40 kV and 40 mA. The surface compositions of the materials before soaking were characterized using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra XPS, Japan) with a monochromatic Al K α source (15 mA, 14 kV). The high resolution XPS spectra were analyzed with the CasaXPS software (version 2.2.107).

The microstructure of the sintered material and the surface morphology of the sample before and after immersion in the SBF were characterized by scanning electron microscopy (SEM, Hitachi E3500, Japan) with an energy dispersive X-ray (EDX) attachment. The surfaces of the materials after immersion were examined by low-angle X-ray diffraction with a grazing incident angle of 1° and a scan speed of 0.02 °/s. The chemical structures of the deposits were analyzed using Fourier transform infrared spectroscopy (FTIR, Tensor 27, Bruker, USA) from 4000 to 400 cm⁻¹ in the KBr form.

The pH values of the SBF were monitored by a pH meter (Accumet, Fisher, USA) during sample immersion, and ion concentrations in the fluid were measured using an inductively coupled plasma atomic emission spectroscopy (ICP-AES, Plasma 400, Perkin-Elmer, USA). The fluorine concentrations in the solution were measured using an ion chromatograph (ICS-3000, Dionex, USA) connected to an analyzer (AS18, Dionex, USA).

3 Results

3.1 Microstructural characterisation of the bonding

Fig. 1 shows the cross-section microstructures of the specimens after sintering under different conditions. For the sample processed without external pressure and the silver interlayer, many pores were observed in the interface region between Ti5FA and Ti6Al4V (Fig.1(a)) and apparent gap existed between Ti10FA and Ti6Al4V (Fig. 1(b)). When the silver interlayer was employed, the original silver interlayer disappeared after sintering and some bright dots appeared in the cross-sections. Also, the composites close to the interface showed more densification. With the use of silver interlayer, the pore density in the interface region between Ti5FA and Ti6Al4V decreased (Fig. 1(c)), while the gap between Ti10FA and the substrate were still present (Fig. 1(d)). On the other hand, the application of an external pressure has led to significant improvement in bonding between the composites and the substrate, especially for Ti10FA. Even without the silver interlayer, only a few pores existed in the interface region between Ti/FA composites and Ti6Al4V for the sintered samples (Fig. 1(e) and 1(f)). These results indicate that external pressure is critical for achieving a sound bonding between the Ti/FA composite and the Ti6Al4V substrate. Furthermore, a sound and defect-free bonding between the composites and Ti6Al4V was achieved after sintering under the external pressure along with a silver interlayer (Fig. 1(g) and 1(h)). The inset EDX patterns in Figs. 1(g) and 1(h) show that Ca, P and Ag were preserved in the structure. Judging from the relative intensity of the peaks, the T10FAT sample contained higher concentrations of Ca and P than the T5FAT sample.

Fig. 1 SEM micrographs of the cross section of the specimens (left: Ti5FA on Ti6Al4V; right: Ti10FA on Ti6Al4V) sintered under various conditions: (a) and (b) without

pressure or Ag; (c) and (d) with Ag interlayer but without external pressure; (e) and (f) with external pressure but without Ag interlayer; (g) and (h) with both Ag interlayer and external pressure (A: substrate; B: interface; C: composite)

Fig. 2 shows the EDX maps of element distributions near the interface in T10FAT. The distribution of Ti showed no discontinuities in the interface region. The diffusion of Al from the Ti6Al4V substrate to the composite occurred during sintering, confirming the formation of a transition band in the interface region (Fig. 2(c)). The bright dots in the cross-section were identified as Ag-rich regions and most were dispersed in the composite, indicating that Ag mainly diffused from the interface to the composite side. By comparing Fig. 2(e) and Fig. 2(f), it could be noticed that the P-rich regions covered more areas than the Ca-rich regions, implying the decomposition of FA and loss of Ca from the material during sintering and cleanse.

Fig. 2 Elemental distributions in the interface area of T10FAT mapped by EDX: (a) SEM micrograph; (b) Ti; (c) Al; (d) Ag; (e) Ca; (f) P

3.2 Phases in the sintered composites

Fig. 3 shows the XRD patterns of the samples before and after sintering. The predominant peaks in the patterns of the as-compacted samples were attributed to Ti (JCPDS 44-1294). Peaks of FA were visible in T5FAT pattern and they were distinguishable in T10FAT pattern. After sintering, the Ti peaks still dominated the XRD patterns, but the FA peaks disappeared. Some new weak peaks emerged in the patterns

and their relative intensities increased with the FA addition in the composite. These peaks were assigned to CaO and Ti phosphides, as the reaction products of Ti with FA during sintering.

Fig. 3 XRD patterns of T5FAT and T10FAT before and after sintering: T5FAT before (a) and after (c) sintering; T10FAT before (b) and after (d) sintering

3.3 Surface characterization of the composite

Fig. 4 shows the XPS surveys of the composite surfaces. The detected elements on the surface included Ti, Ca, Ag, C, N, and O, while no P was present. The C 1s peak and the N 1s peak in the spectra were attributed to contamination during exposing to air and handling [31]. To identify the valence status, the key elements were further characterized by high resolution XPS scanning and the obtained spectra were deconvoluted as shown in Fig. 5.

Fig. 4 The XPS survey of the composite surfaces: (a) T5FAT; (b) T10FAT

The Ti 2p spectra of T5FAT and T10FAT were very similar in shape and both were decomposed into several components (Fig. 5(a1) and (b1)). The two dominant deconvoluted peaks at the binding energies of 459.1 eV and 464.8 eV were attributed to the 2p_{3/2} and 2p_{1/2} spectra of Ti⁴⁺ respectively, showing that Ti mainly existed as TiO₂ on the surface [32, 33]. The small peak at the binding energy of 453.9 eV was assigned to the 2p_{3/2} spinning of metallic Ti, which implied the presence of Ti metal on the surfaces

as well [34]. Furthermore, the deconvolution of Ti 2p_{3/2} peak revealed two subpeaks at binding energies of 456.1 eV and 457.7 eV, corresponding to the position of 2p_{3/2} spectra of Ti²⁺ and Ti³⁺ respectively [35]. Therefore, it could be concluded that both Ti metal and Ti suboxides were present on the composite surface in addition to the major oxide TiO₂.

Fig. 5 High resolution XPS spectra of the elements on the composite surfaces and the corresponding deconvolution: (a1-a4) T5FAT; (b1-b4) T10FAT

The O 1s spectrum is generally fitted with oxygen in three statuses, oxides (O²⁻), hydroxide (OH⁻), and water (H₂O) [36]. The O 1s spectrum in Fig. 5 show a primary peak at the binding energy of 530.5 eV, which corresponded to the O 1s position of lattice oxides [35, 36]. The dominance of this peak implied that the oxygen on the surface was mainly in the form of oxides. The second strongest peak in the spectrum presented at the binding energy of 532 eV, assigned to the OH⁻ group on the surface. The peak due to absorbed water appeared at 533 eV. Quantitative analysis demonstrated that the calculated concentration of oxygen in OH⁻ group on T10FAT surface was 52%, substantially higher than the 36% on T5FAT surface. Also, the percentage of oxygen in chemisorbed water on T10FAT surface was about double of that on T5FAT surface (15.8% vs. 7.6%).

The high resolution Ca 2p spectra show a typical doublet peak feature and both the Ca 2p_{3/2} and Ca 2p_{1/2} peaks were symmetrical. The binding energy difference between the two peaks was 3.6 eV, indicating that Ca²⁺ species were contained on the surface [37]. In

both of the Ag 3d spectra, there were two symmetrical peaks at the binding energies of 368.4 eV and 374.4 eV. The two peaks were assigned to 3d_{5/2} and 3d_{3/2} spinning of metallic Ag, suggesting that only metallic silver was present on the surface [38, 39].

3.5 Surface morphologies of the composite after immersion into SBF

Figs. 6 and 7 show the surface morphologies of T5FAT and T10FAT before and after immersion in the SBF for various periods of time. Before immersion, both surfaces contained many micron-scaled pores and uniformly distributed polishing grooves. After 8-hr immersion in the SBF, most pores on the T5FAT surface became invisible due to the coverage by numerous spherical particles precipitated from the fluid. For T10FAT, most of the surface area has been covered by the spongy aggregation of spherical particles. With the increase of the immersion time, the nucleation and growth of the precipitate continued. As a result, more and more globular particles were deposited on the T5FAT surface and the entire surface was covered by a layer of precipitates after 7 days. The precipitates became denser as the soaking time increased. On the T10FAT surface, the precipitation layer became thicker and denser with the immersion time and the composite surface was completely coated after soaking in the SBF for 3 days. Further increase in immersion time did not lead to significant changes to the surface morphology. By comparing Fig. 6 and Fig. 7, it can be drawn that the T10FAT sample could induce more precipitates onto the surface than T5FAT for the same immersion time.

Fig. 6 SEM micrographs of T5FAT surface after immersion in the SBF for various times:

(a) 0 hr; (b) 8 hrs; (c) 1day; (d) 3days; (e) 7 days; (f) 14 days

Fig. 7 SEM micrographs of T10FAT surface after immersion in the SBF for various times: (a) 0 hr; (b) 8 hrs; (c) 1day; (d) 3days; (e) 7 days; (f) 14 days

3.6 Precipitates formed on the composite surface from the SBF

Fig. 8 shows the XRD patterns of the composite surface after immersion in the SBF for various periods of time. During the immersion, only apatite and the Ti peaks from the substrate were present in the patterns of T5FAT surface. Even though the relative intensities of the apatite peaks became stronger with the increase of immersion time, the Ti peaks dominated the patterns for up to 7 days of immersion. After 14 day immersion, the predominant crystal phase on T5FAT surface was changed to be apatite. A similar trend was also observed in the T10FAT surface. In addition to the apatite and the substrate, calcium carbonate (CaCO_3) was detected on T10FAT surface after 1 day immersion in the SBF. With the increase of immersion time, the CaCO_3 peaks weakened and they vanished from the pattern after 14 days.

Fig. 8 Low-angle XRD patterns of the precipitated layers on the composite surface after soaking in SBF for various times: (a) T5FAT; (b) T10FAT; (T: Ti; A: apatite; C: CaCO_3)

The FTIR spectra of the precipitate formed on the composite surface during soaking in the SBF are shown in Fig. 9. All the spectra corresponded to the characteristic spectrum of the bone-like carbonated apatite [40]. The strong absorption region at 3700 to 3000 cm^{-1} and the band at 1638 cm^{-1} were assigned to O-H stretching and bending in H_2O ,

respectively [41]. The most intense band in the spectra was located from 1200 to 960 cm^{-1} , assigned to the P-O asymmetric stretching mode (ν_3) of the PO_4^{3-} group [42]. The single band in the range from 670 cm^{-1} to 500 cm^{-1} , or the doublet at 603 cm^{-1} and 565 cm^{-1} , was from the triply degenerated bending modes (ν_4) of phosphate O-P-O bonds [43]. Another broad band from 1600 to 1400 cm^{-1} and the small sharp peak at 874 cm^{-1} were attributed to the characteristic band of the CO_3^{2-} group in the carbonated apatite [44, 45]. With the increase of soaking time, the relative intensity of the bands due to CO_3^{2-} group was improved, indicating that more carbonate groups were coupled in the apatite. Also, as demonstrated by the transformation of the single ν_4 region of PO_4^{3-} to a doublet, the crystallinity of the formed apatite was improved with the increase of immersion time.

Fig. 9 FTIR spectra of the precipitates formed on the composite surface after soaking in SBF for various times

3.7 Characteristics of the SBF solution during soaking

Fig. 10 shows the variations of pH values and ion concentrations in the solution during the immersion of the material. In general, the measured parameters for the solutions containing different samples displayed many similarities. The change of the parameters mainly occurred in the first week of immersion, after which the values became stable. For both solutions, the pH value increased rapidly at the beginning until it reached a maximum value on the third day, and it then dropped subsequently until it stabilized after 1 week. For the same soaking time, the pH value of the solution containing T10FAT was higher than that containing T5FAT. With the increase in the immersion time, both the F

and Ag concentrations in the solutions increased continuously, while the P concentrations decreased over time.

The major difference between the two solutions is the change in Ca concentration. For the solution containing T10FAT, the Ca concentration increased initially with time until the third day of immersion, and then it decreased with further immersion. In contrast, the Ca concentration decreased continuously over time in the SBF containing T5FAT, and it was lower than that in the solution containing Ti10HAT for the same immersion time.

Fig. 10 Variations of pH value and the concentration of calcium, phosphorous, fluorine and silver in the SBF with the soaking time

4 Discussion

The microstructures in the bonding interface region demonstrated that external pressure and the silver interlayer have critical effect on the bonding quality (Fig. 1). Without the external pressure and the silver interlayer, poor bonding between the Ti/FA composite and the Ti6Al4V substrate was observed, as evidenced by the high density of pores and cracks in the interface (Fig. 1 (a) and (b)). Applying an external pressure during sintering could help to maintain a close contact between the composite and the substrate, leading to considerable improvement of the bonding quality (Fig. 1(c) and (f) vs. Fig. 1(a) and (b)). Because FA in the mixture adversely influenced the joining of Ti powders to Ti6Al4V, applying an external pressure alone could not completely eliminate the inherited defects such as pores and cracks in the interface region. As shown in Fig. 1(c) and (d), a silver interlayer placed between the substrate and the composite could improve

the soundness of the bonding between the Ti/FA composites and the substrate. However, using a silver interlayer alone without the application of external pressure could not produce a sound bonding between the composite and the substrate either. A defect-free interface was achieved only with the application of both a silver interlayer and an external pressure.

The mechanism with which silver interlayer influenced the bonding process in this study is expected to be significantly different from that used in diffusion bonding [21]. In the diffusion bonding process, the key role that the silver interlayer played is to facilitate the joining of the two metals by solid phase diffusion at a processing temperature below the melting point of silver (700–850 °C). While in the current cladding process, the processing temperature was higher than the melting point of silver and a liquid silver phase was involved in the bonding treatment. The formation of molten silver would not only fill the gaps between Ti6Al4V substrate and the Ti/FA composite, but also facilitate the rearrangement of the particles in the composite [45]. Both of these mechanisms will be beneficial for the densification of the composite powders near the interface and improve the bonding between the composite and the substrate. However, the bonding improvement by the assistance of liquid silver alone during pressureless sintering could not completely eliminate the defects, probably due to the non-favourable wetting of metallic silver with ceramic FA.

XPS analysis revealed that Ag existed in the metallic state in the sintered materials. The metallic silver in the samples can react with the SBF and release silver ions to the surrounding environment, as indicated by a constant increase in Ag^+ concentrations in the SBF after immersion of the samples over time (Fig.10 (e)). The released silver ions can

provide antibacterial and bactericidal functions by damaging the bacterial RNA and DNA in the body environment [24, 46]. This will provide added benefits for biomedical implant applications.

FA itself could react with the trace water in Ar at a temperature below 900 °C according to the following equation [47]:

The substitution of OH⁻ for F in the FA structure leads to the formation of hydroxyafluorapatite (HFA) and the release of fluorine from FA. In the presence of Ti, the hydroxyfluorapatite (HFA) could further decompose during sintering to form mainly CaO and Ti phosphides (Fig. 3) [10, 48]. Because the FA concentration in the composite was low, the above reactions could consume a majority of the FA in the composite. Such reactions might be the reason why the positions of P-rich regions and Ca-rich regions did not match in the EDX element mapping (Fig. 2).

The essential requirement for an implant to bond to living bone is the formation of bone-like apatite on its surface when implanted in the living body and the *in vivo* apatite formation can be reproduced in a SBF [29]. After immersion in the SBF, the bone-like carbonated apatite was formed on the material surface, as identified by XRD and FTIR (Figs. 8 and 9). In addition to apatite, CaCO₃ was also formed on T10FAT surface at the early stage of immersion. Because CaCO₃ is biodegradable and biocompatible, the formation of CaCO₃ is not expected to bring any adverse biological effect. Therefore, both T5FAT and T10FAT were bioactive and they had the ability to induce the bone-like apatite formation on their surface in the physiological environment, even though the concentration of FA in the composites is relatively low.

Because the surface condition determines the direct response of the implant to the physiological environment, it is rational to reckon that the bioactivity of the material is more associated with the surface functional group within the outmost surface [36, 49]. In contrast to normal Ti^{4+} on the nature Ti surface, the high resolution XPS spectra indicated that Ti was presented as multiple states on the composite surface, including Ti^0 , Ti^{2+} , Ti^{3+} and Ti^{4+} . The non-stoichiometric Ti oxide on the surface are more active than TiO_2 in the physiological environment and represent a range of possibilities regarding chemical bond coordination between the implant surface and the adjacent biomolecules [50]. The Ti suboxides were easy to react with water molecules in air or in aqueous solutions and formed Ti-OH groups as,

The Ti-OH groups can induce apatite nucleation through static electropotential interactions with the positively charged Ca ions in the fluid [36, 51]. In addition, the preserved Ca on the composite surface could act as nuclei and lead to an effective initial deposition of the apatite from the solution [52]. Once the apatite nuclei were initiated, they could propagate spontaneously by consuming the calcium, phosphate and carbonate ions from the surrounding fluid and foster the growth of carbonated apatite [53].

Furthermore, the CaO phase as the FA decomposition product in the material could also promote the apatite formation. After immersion in the SBF, CaO would react with water in the fluid as follows:

This reaction led to the increase in the pH value and Ca^{2+} concentration in the fluid at the early stage (Fig. 10). On one hand, the Ca^{2+} released from the composite would improve

the degree of Ca^{2+} supersaturation near the surface, which could decrease the free energy for nucleation and growth of apatite [54]. On the other hand, the increased pH value of the fluid was kinetically suitable for the apatite precipitation process [55]. Both effects were favourable for the nucleation and growth of carbonated apatite.

Because of a higher CaO amount in T10FAT than in T5FAT, more OH^- and Ca^{2+} were generated by the hydration reaction (4) after immersed into the SBF, which lead to a higher pH value and Ca^{2+} concentration in the fluid containing T10FAT (Fig. 9). This factor also contributed to the faster apatite formation on T10FAT surface than on T5FAT after immersion (Figs.6 and 7). Due to the formation of apatite and less Ca^{2+} released from the composite, both the Ca^{2+} and PO_4^{3-} concentration in the SBF containing T5FAT decrease continuously after immersion. In contrast, the initially increase of Ca^{2+} concentration in the fluid containing T10FAT indicated that more Ca^{2+} ions were released from T10FAT than those consumed by apatite formation at the early stage of immersion. In the vicinity of T10FAT surface, after the consumption of the local HPO_4^{2-} for the apatite formation, some excessive Ca^{2+} ions would react with the HCO_3^- in the SBF to form CaCO_3 [44]

Due to the fact that the HCO_3^- concentration in human plasma is more than 6 times higher than that in the SBF, formation of CaCO_3 due to higher Ca^{2+} release from the implant is expected after *in vivo* implantation [56].

Release of fluorine ions from the material after immersion in the SBF indicated that some of F was still preserved in the composite even though some has been removed from FA due to reaction (2). The fluorine ions were expected to promote the mineralization

and crystallization of calcium phosphate in the bone forming and resist the attack of caries in oral environment [5-9]. Because the decomposition of FA was related to the reaction between FA and water trace in the gas atmosphere, the sintering process in a sealed environment, such as the HIP process, would possibly be helpful to inhibit the occurrence of the decomposition and preserve the fluorine in the material.

5 Conclusions

Ti/FA composites were successfully joined to Ti6Al4V substrate. Applying a silver interlayer and an external pressure during sintering was critical for achieving the defect-free interface between the composite and the substrate. The fabricated materials were bioactive to induce the formation of bone-like carbonated apatite after immersion in the SBF for a short time. Furthermore, the materials could release silver and fluorine ions, which could impart favourable effects in the physiological environment after the implantation. Therefore, the described cladding process provides a promising route to promote the bioactivity of Ti alloys with more valuable functionalities to be used as hard tissue implants.

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Fig. 1 SEM micrographs of the cross section of the specimens (left: Ti5FA on Ti6Al4V; right: Ti10FA on Ti6Al4V) sintered under various conditions: (a) and (b) without pressure or Ag; (c) and (d) with Ag interlayer but without external pressure; (e) and (f) with external pressure but without Ag interlayer; (g) and (h) with both Ag interlayer and external pressure (A: substrate; B: interface; C: composite)

Fig. 2 Elemental distributions in the interface area of T10FAT mapped by EDX: (a) SEM micrograph; (b) Ti; (c) Al; (d) Ag; (e) Ca; (f) P

Fig. 3 XRD patterns of T5FAT and T10FAT before and after sintering: T5FAT before (a) and after (c) sintering; T10FAT before (b) and after (d) sintering

Fig. 4 The XPS survey of the composite surfaces: (a) T5FAT; (b) T10FAT

Fig. 5 High resolution XPS spectra of the elements on the composite surfaces and the corresponding deconvolution: (a1-a4) T5FAT; (b1-b4) T10FAT

Fig. 6 SEM micrographs of T5FAT surface after immersion in the SBF for various times:

(a) 0 hr; (b) 8hrs; (c) 1day; (d) 3days; (e) 7 days;(f) 14 days

Fig. 7 SEM micrographs of T10FAT surface after immersion in the SBF for various times: (a) 0 hr; (b) 8 hrs; (c) 1day; (d) 3days; (e) 7 days;(f) 14 days

Fig. 8 Low-angle XRD patterns of the precipitated layers on the composite surface after soaking in SBF for various times: (a) T5FAT; (b) T10FAT; (T: Ti; A: apatite; C: CaCO_3)

Fig. 9 FTIR spectra of the precipitates formed on the composite surface after soaking in SBF for various times

Fig. 10 Variations of pH value and the concentration of calcium, phosphorous, fluorine and silver in the SBF with the soaking time