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Cladding of titanium/hydroxyapatite composites onto Ti6Al4V for load-bearing implant applications

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Abstract

To improve the bioactivity of Ti6Al4V for use as a load-bearing hard tissue replacement, titanium/hydroxyapatite (Ti/HA) composites were bonded to a Ti6Al4V substrate by a novel cladding method. With the aid of a silver foil as the interlayer and an external pressure during sintering, the interfaces between the composites and the substrate were free of defects. The bioactivity of the fabricated materials was evaluated in the simulated body fluid (SBF) and the results demonstrated that the materials could induce nucleation and growth of bone-like apatite in the SBF. Factors contributed to the bioactivity of the materials were discussed. The release of Ag^+ ions from the materials was also detected, which is expected to impart antibacterial effect after implantation, and further enhance the functionalities of the materials.

Keywords: Titanium, hydroxyapatite, simulated body fluid, cladding

1 Introduction

Due to its good biocompatibility and excellent mechanical properties, Ti6Al4V is widely used in dentistry and orthopedic replacement [1-2]. However, Ti6Al4V is a bioinert material which can not induce biological fixation to the surrounding tissues after implantation [3]. To improve the bioactivity of the alloy and enhance the implant-tissue osseointegration, various attempts have been made to modify the surface of the alloy, such as anodization [4, 5], coating [6, 7], ion-implantation [8] and chemical etching [9]. Among these attempts, hydroxyapatite (HA) coating on Ti6Al4V is the most successful approach and commonly used in medical applications [10]. Because of the

significant differences in the chemical and physical properties between the coating and substrate, many defects, such as cracks and voids, would present in the interface, resulting in an early degradation and failure of the implant [11]. Furthermore, most of the coating methods are conducted by costly facilities, which also limit the accessibility of the techniques.

Diffusion bonding is a solid state joining process used for similar or dissimilar materials, without causing gross microscopic distortion [12, 13]. During diffusion bonding, two clean surfaces are brought into contact with each other under vacuum or an inert atmosphere at a temperature lower than the melting point of the base material [14]. An interlayer with low melting point, such as silver, is sometime used to facilitate the bonding process [15, 16]. An additional benefit of adding silver into implantable materials is that silver could render broad-spectrum antimicrobial property, which is particularly significant for the polymicrobial colonization associated with biomaterial related infections [17]. Silver itself is neither genotoxic nor cytotoxic as compared to other widely used metal implants [18]. When it reacts with the body fluids, the released silver ions can damage bacterial RNA and DNA, thus inhibiting their replication [19]. Therefore, both metallic and ionic silver have been incorporated into the biomaterials such as polyurethane, hydroxyapatite and bioglasses [17, 20-22].

The Ti/HA composites fabricated by powder metallurgy could circumvent the inherent disadvantages of the coating methods and they were proved to be biocompatible and bioactive both *in vitro* and *in vivo* [23-27]. Because the mechanical properties of the composite, especially bending strength and fracture toughness, decrease markedly with the increase of HA addition, Ti/HA composites may not have sufficient mechanical

properties for some load-bearing applications [28]. Cladding bioactive Ti/HA composites with a low concentration of HA addition onto the Ti6Al4V substrate can potentially satisfy both mechanical and biological requirements for the heavy load-bearing hard tissue replacement.

In this study, an innovative cladding method using silver as an interlayer was developed to bond Ti/HA composites to Ti6Al4V. Both the interface and surface of the material were characterized and the bioactivity of the material was evaluated in the simulated body fluid (SBF).

2 Experimental procedures

2.1 Preparation of the composites

Ti6Al4V (RMI Titanium Company, Mississauga, Canada) samples with dimensions of 8 mm×8 mm×1.7 mm were cut from a 1.7 mm thick plate. 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. The Ti/HA composites were fabricated from commercially pure Ti powder (Atlantic Equipment Engineers, USA) and HA powder (Pentax, Japan). Ti/HA powder mixtures with 5 and 10 vol.% HA were first prepared by mixing the powders in a 3D mixer (Laval Lab, Canada) for 48 hrs in argon atmosphere.

The silver foil (Alfar Aesar, USA) used as the interlayer was 25 µm thick. A single layer of silver foil was placed on top of the polished surface of the Ti6Al4V substrate, and the sample was placed inside of a rigid tool-steel die. An appropriate amount of the Ti/HA mixture was then placed on top of the polished surface of the Ti6Al4V sample

inside the die, and a uniaxial pressure of 350 MPa was applied to compact the Ti/HA mixtures onto the Ti6Al4V substrate. The compacted sample was sintered in argon atmosphere at 1000 °C for 1 hr under a 0.1 MPa uniaxial load. For convenience, the sample with X volume percentage of HA was denoted as TXHAT.

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

To evaluate the bioactivity of the composite, the SBF solution with ion concentrations close to human blood plasma was prepared following the procedures used by Kokubo et al. [29]. Because SBF can be easily contaminated by bacteria even after short time exposure to the ambient environment [30], 1g/l NaN₃ was added to the solution in this study to inhibit the growth of the anaerobic bacteria and maintain the ion concentrations in the solution. The ion concentrations in the SBF and the blood plasma were listed in Table 1.

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

The as-sintered composite samples were polished with sandpapers up to 1200 grit and then washed ultrasonically in acetone, ethanol and deionised water for 10 minutes each. The cleaned samples were dried with a heating gun and then soaked into the SBF. After soaking for various periods of time, the samples were gently rinsed with deionised water, and naturally dried in a fume hood.

2.3 Characterizations

The phases in the sintered samples were detected by X-ray diffraction (XRD; X'Pert, Philips, Netherlands) using Cu K α radiation, with an acceleration voltage of 40 kV and a filament current of 40 mA. The surface compositions of the composites before soaking in the SBF were characterized using X-ray photoelectron spectroscopy (XPS; Kratos Axis Ultra XPS, USA) with a monochromatic Al K α source ($h\nu=1486.6$ eV, 15mA, 14 kV). The XPS spectra were analyzed with the CasaXPS software (version 2.2.107).

The surface morphology of the samples before and after immersion in the SBF was characterized by scanning electron microscopy (SEM; Hitachi E3500, Japan) with an energy dispersive X-ray (EDX) analyzer. The pH values and ion concentrations of the SBF were monitored by a pH meter (Accumet, Fisher, USA) during sample immersion, and measured using an inductively coupled plasma atomic emission spectroscopy (ICP-AES; Plasma 400, Perkin-Elmer, USA).

The precipitated phases on the composite surfaces 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 depositions were analyzed by Fourier transform infrared spectroscopy (FTIR; Tensor 27, Bruker, USA) from 4000 to 400 cm⁻¹ in the KBr form.

3 Results

3.1 Characteristics of the interface area

Fig. 1 shows the cross-section microstructures of the specimens after sintering. The micrographs displayed that the interface region between the composites and the Ti6Al4V substrate were sound and defect-free. The silver interlayer could not be identified from

the interface area, while many bright dots were dispersed in the composite side. Three regions could be observed in the vicinity of the interface area: the solid Ti6Al4V substrate, a dense transition band, and the porous composite. The inset EDX patterns in Figure 1 show that Ca, P and Ag were preserved in the structure. Judging from the relative intensity of the peaks, the T10HAT sample contained higher concentration of Ca and P than the T5HAT sample.

Fig. 1 *SEM micrographs of the cross section of the specimen after sintering*
(a) T5HAT; (b) T10HAT; (c) T5HT; (d) T10HT

Fig. 2 shows the EDX element distribution maps for T5HAT near the interface. The distribution of Ti showed that there were no discontinuities in Ti concentration in the structure, as expected. Diffusion of Al from the Ti6Al4V substrate towards the interface was noticeable in the transition band. Fig.2 (d) showed that the bright dots were Ag-rich, indicating that Ag 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 did not match with the Ca-rich regions, indicating that HA has already decomposed after sintering.

Fig. 2 *Elemental distributions in T5HAT near the interface mapped by EDX: (a)*
micrograph of the site; (b) Ti; (c) Al; (d) Ag; (e) P; (f) Ca

3.2 Phases in the sintered composites

Fig. 3 shows XRD patterns of the composite samples after sintering. For both T5HAT and T10HAT samples, the predominant peaks are from Ti (JCPDS 44-1294). A number of weak peaks were observed in the samples. Due to the very low intensity of the peaks, it is difficult to determine the phases with high confidence. Given that the position of the peaks matches that of CaO and titanium phosphides, respectively, and the relative intensities of the peaks increased with the HA addition in the composite, these weak peaks probably indicate the formation of CaO and titanium phosphides. However, there was no peaks corresponding to HA or Ag could be detected.

Fig. 3 *XRD patterns of T5HAT and T10HAT after sintering*

3.3 XPS characterization of composite surface

The XPS surveys of the composite surfaces are shown in Fig. 4. The detected constituents included Ti, Ca, Ag, O and C, while no P was revealed. The relatively strong C signal was most likely due to surface contamination by adsorbed organic molecules, which is not unusual for surfaces exposed to air [31]. To identify the valence status of the key elements, high resolution XPS scanning was employed and the spectra were deconvoluted, as shown in Fig. 5.

Fig. 4 *XPS survey spectra of the composite surfaces*

The Ti 2p bands for the two composites were similar in shape (Fig. 5(a1) and (b1)). As shown in the deconvolution, there were three major component peaks at the binding energy of 464.8 eV, 459.0 eV, and 453.9 eV, respectively. The first two were the

dominant peaks in the spectra and they were attributed to 2p_{1/2} and 2p_{3/2} peaks of Ti⁴⁺, indicating that Ti was mainly presented as TiO₂ on the surface. The peak at 453.9 eV was assigned to Ti metal 2p_{3/2}. Besides, some weak peaks appeared at the binding energy of 463.4 eV, 457.7 eV, 456 eV, and 461.5 eV. The first two were due to the doublets of Ti³⁺ 2p and the last two were attributed to Ti²⁺ 2p [32]. Therefore, it can be deduced that Ti suboxides and Ti metal were also present on the composite surface in addition to TiO₂.

The O 1s spectrum was resolved into three subpeaks of oxygen: (1) in oxides (O²⁻, ~530.5 eV), (2) in hydroxide group (OH⁻, ~532.0 eV), and (3) in chemisorbed water (H₂O, ~533.2 eV), as demonstrated in Fig. 5 [33]. In the spectrum of O 1s for T5HAT, the calculated amount of oxygen in OH⁻ group was 47.6 at.%, slightly less than the amount of oxygen in oxides (49.2 at.%). However, in the O 1s spectrum for T10HAT, the concentration of oxygen in OH⁻ group was 48.3 at.%, significantly higher than the 33.7 at.% in oxides. Furthermore, the amount of the chemisorbed water discovered in the O 1s spectrum was substantially higher in T10HAT surface than in T5HAT surface (17.8 at.% vs. 3.2 at.%).

Fig. 5 *The high resolution XPS spectra of the elements on the composite surfaces and the corresponding deconvolution: (a1-a4) T5HAT; (b1-b4) T10HAT*

The high resolution spectra of Ca 2p have a typical doublet peak feature with a spin orbit splitting of 3.6 eV [34, 35]. Both Ca 2p_{3/2} and Ca 2p_{1/2} spectra were symmetrical in the spectra. Because of the insensitivity of the core level spectrum Ca 2p toward variation in chemical environment, the Ca species identification could not be

accomplished with the XPS information alone [36]. Taking into consideration of the reactions between HA and Ti during sintering, the Ca might exist in various phases, such as CaO and CaTiO₃, in the composite.

The Ag 3d spectra of the composites are shown in Fig. 5(a4) and 5(b4). In both spectra, the binding energy of Ag 3d_{5/2} was 368.4eV with a difference of 6 eV in binding energy between the Ag 3d_{5/2} and 3d_{3/2} peaks, suggesting that the silver existed in the metallic state in both materials [37, 38].

3.4 Surface morphologies of the composite after immersion in the SBF

The surface morphologies of T5HAT before and after immersion in the SBF for various times are shown in Fig. 6. Before immersion, the composite surface was featured by uniformly distributed micron-scale pores and polished grooves. After 8-hr immersion, many globular particles dispersed on the composite surface and most pores became invisible due to the coverage of the newly formed deposition. With the increase of the immersion time, the nucleation and growth of the precipitate continued. As a result, more and more globular particles deposited on the surface, and the individual particles grew to form agglomerates over time. The surface was entirely covered by a porous layer of precipitates after 3 days. However, further increase of immersion time did not lead to significant changes to the morphology of the surface.

Fig. 6 *Surface morphologies of T5HAT before and after immersion in the SBF for various times: (a) before immersion; (b) 8 hrs; (c) 1day; (d) 3days; (e) 7 days; (f) 14 days*

Fig. 7 shows the SEM surface micrographs of T10HAT before and after immersion in the SBF. The original composite surface contained many open pores and polished grooves (Fig. 7(a)). After soaking in the SBF for 8 hr, numerous small particles were deposited on the surface (Fig. 7(b)). With the increase of the immersion time, more globular particles were precipitated and groups of aggregated spheres were dispersed on the surface (Fig. 7(c)). The precipitation layer grows in thickness over time, but the surface morphology remained more or less the same after 3 days. By comparing with Fig. 6, it could be observed that for the same length of immersion time, the T10HAT samples has more precipitates on the samples surface.

Fig. 7 *Surface morphologies of T10HAT before and after immersion in the SBF for various times: (a) before immersion; (b) 8 hrs; (c) 1day; (d) 3days; (e) 7 days; (f)14 days*

3.6 Phases formation on the surface of samples after immersion in SBF

Fig. 8 shows the XRD patterns for the surface of the composite samples after immersion in the SBF for different lengths of time. For the T5HAT samples, only apatite and the substrate peaks were present in the patterns, and the relative intensity changed with the exposure time. After 1 day soaking, the peaks for the apatite were very weak and the predominant peaks were from the Ti substrate. This is consistent with the SEM observation that the surface of the samples was only partially covered by the precipitates after 1 day of immersion in the SBF. After 3 days, the apatite peaks became dominated in the XRD pattern and the substrate peaks became significantly weaker. Similar trend was also observed in the XRD patterns of the T10HAT surface during soaking in the SBF

(Fig. 8(b)). Besides apatite, CaCO_3 was also identified in the XRD patterns of T10HAT after 1 day immersion in the SBF. With the elongation of soaking time, the intensities of the calcite peaks decreased and the peaks disappeared from the pattern after 1 week immersion in the SBF.

Fig.8 XRD patterns of the precipitated layers on the composite surface after soaking in SBF for various times: (a) T5HAT; (b) T10HAT; (T: Ti; A: apatite; C: CaCO_3)

The FTIR spectra of the precipitates collected from the surface of the samples immersed in the SBF are summarized in Fig. 9. All the characteristic peaks are attributed to carbonated apatite [39, 40], indicating the formation of bone-like apatite on the samples surface during immersion in SBF. The broad absorption bands at 3450 cm^{-1} and 1638 cm^{-1} were assigned to O-H stretching and bending of H_2O , respectively [41]. The most intensive band in the region from 1200 to 960 cm^{-1} was assigned to the P-O asymmetric stretching mode (ν_3) vibration of the PO_4^{3-} group [42]. Another strong peak, or the doublet, located in $550\text{-}650\text{ cm}^{-1}$, was derived from the triply (ν_4) degenerated bending modes of phosphate O-P-O bonds [43]. The broad band in the region from 1400 to 1600 cm^{-1} and a sharp peak at 874 cm^{-1} were attributed to the CO_3^{2-} group in the carbonated apatite [44]. With the elongation of the immersion time, the bands assigned to CO_3^{2-} group became stronger, indicating that more carbonate groups were coupled in the apatite. Also, the improvement of the apatite crystallinity was demonstrated by the transformation of the single band in ν_4 region of PO_4^{3-} to a doublet. Besides the bands due to carbonated apatite, the shoulder at 712 cm^{-1} appeared in the spectrum of the precipitate

formed on T10HAT after 1 day immersion, which was attributable to calcium carbonate (CaCO_3) [45]. However, this band vanished from the FTIR spectra after a longer exposure time in the SBF.

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

3.6 Changes in pH value and ion concentration of SBF solution during soaking

Variations of pH value and ion concentrations in the SBF during the immersion of the composites are displayed in Fig. 10. The change of the pH value over time for the SBF solution containing the T5HAT sample is similar to that containing the T10HAT sample. In both solutions, the pH value increased rapidly at the beginning of immersion until it reached maximum value on the third day. The pH value dropped subsequently until it stabilized after 1 week. The SBF containing T10HAT had a higher pH value than the SBF containing T5HAT for the same length of immersion time.

The change in ion concentrations in the two SBF solutions also showed many similarities. These include continued decreasing in P concentration and increasing in Ag concentration over time, and essentially the same concentration of P and Ag for the same length of immersion time. The major difference between the two solutions is the change in Ca concentration. For the solution containing T10HAT, the Ca concentration increased initially with time until it reached a maximum after 3 days of immersion, The Ca then decreased with time. In the SBF solution containing T5HAT, on the other hand, the Ca concentration decreased continuously over time, and is overall lower than the solution containing T10HAT for the same immersion time.

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

4 Discussion

Silver has been used as an interlayer to join pure Ti to carbon steel by diffusion bonding [16]. Due to the low processing temperatures (700–850 °C) used in the previous work, the silver layer remained in the interface and there was essentially no phase transformation or macrostructural changes to silver during diffusion bonding. In the current cladding process, the processing temperature was higher than the melting point of Ag, indicating the involvement of liquid phase of Ag during the bonding treatment. Because there were open pores in the composite, molten Ag would be more readily diffuse into the Ti/HA composite than into the solid TiAl6V4 substrate. The formation of molten Ag is expected to not only fill the gaps between the titanium substrate and the Ti/HA composite, but also facilitate the rearrangement of the particles in the composite. Both of these mechanisms could improve densification of the composite near the interface and promote the bonding between the composite and the substrate. Therefore, the Ag interlayer is considered critical for the formation of defect-free interface layer.

XPS spectra revealed that Ag is present in metallic status in the sintered materials, indicating that it did not take part in any chemical or metallurgical reactions during sintering. The metallic silver in the sintered materials, however, 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 sintered samples over

time. The silver ions thus formed in the body environment can inhibit the replication of bacteria by damaging their RNA and DNA [19], and provide antibacterial and bactericidal functions [46].

As shown in the insets of Fig. 1, Ca and P were both present in the sintered samples. The stronger Ca and P peaks in the T10HAT sample as compared with those in the T5HAT sample were due to the higher HA addition in the composite. It is known Ti accelerates the decomposition of HA at elevated temperatures [47, 48]. The absence of HA peaks in the material was believed to be the result of HA decomposition during sintering. This was supported by the evidence that the position of P-rich regions and Ca-rich regions did not match in the EDX element mapping, as shown in Fig. 2. Since a major decomposition product of HA is CaO, high concentration of CaO was expected to be observed after HA decomposition. The sparsity of Ca-rich regions in the element map was probably due to the removal of CaO during sample cleanse [23, 47].

During immersion, carbonated apatite was formed on the surface of both T5HAT and T10HAT samples, as revealed by XRD and FTIR (Figs. 8 and 9). In addition, CaCO_3 was also detected on the surface of the T10HAT sample at an early stage of soaking, but it disappeared after the sample was immersed in the SBF for 1 week. Because CaCO_3 is regarded as biodegradable and biocompatible, its temporary existence in the coating would have no undesirable effect on the biological performance of the composite [49, 50, 53, 54].

It is widely accepted that the biological response to the implant will be influenced by the microscopic (atomic level) surface properties of the materials [33]. Tissue response is a result of the short range (<1nm) interactions taking place between the surface groups

and the biological surrounding [51, 52]. Therefore, the bioactivity of the material is more associated with the functional groups within the outmost surface than those in the deep area [33]. On the composite surface, the Ti was presented in multiple valance states, including Ti^+ , Ti^{2+} , Ti^{3+} , Ti^{4+} , and Ti metal, differing from the normal Ti^{4+} condition in Ti materials exposed to air for extended period of time. The complex valence status of Ti was due to the oxygen diffusion from the exterior surface to the inside during sintering. Ti metal and Ti suboxides on the composite surfaces are believed to be more active than TiO_2 in the physiological environment and can activate chemical bonding between the implant surface and adjacent biomolecules [53]. In the SBF, the Ti suboxides can be hydrated to form Ti-OH groups on the surface of the composite in the SBF following the equation:

This hydration process caused the composite surface negatively charged with hydroxyl groups. The SBF with a pH of 7.4 was favourable for the occurrence of the reaction. The positively charged calcium ions would be bound to the surface because of Coulomb's force and the negatively charged groups would be caught through a hydrogen bond or attraction from the cations. Once the enrichment of the ions over the critical level for the nucleation, apatite nuclei were initiated and then propagated spontaneously by consuming the calcium, phosphate and carbonate ions from the surrounding fluid [54, 55].

Furthermore, the formation of the CaO phase in the material could also promote the formation of apatite. After immersion, the CaO would react with the water in the fluid according to equation (3):

The reaction resulted in the increase of pH value and Ca^{2+} ion concentration in the solution at the early stage, as shown in Fig .9. On one hand, the Ca released from the composite according to Eq.(3) would improve the degree of supersaturation near the surface, which could decrease the free energy for nucleation and growth of apatite [56]. On the other hand, the increased pH value of the fluid was kinetically suitable for the apatite precipitation process [57]. 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 [58].

After the immersion of the composite samples, the pH value of the SBF initially increased due to the release of the OH^- groups on the composite surface and further hydration of CaO. The higher pH value and Ca concentration in the SBF containing T10HAT were primarily caused by the higher CaO amount in the composite. For solutions containing the T5HAT sample, the constant decrease in Ca^{2+} concentration over time indicated that the Ca^{2+} ions released from the material were less than those precipitated into the coating. While for the solution containing the T10HAT sample, the initial increase in Ca^{2+} concentration showed that more Ca^{2+} ions were released from the composite than those deposited in apatite due to the higher concentration of HA addition to the sample. However, with the limited amount of CaO in the composite, the release rate of Ca^{2+} would decrease over time and eventually more Ca^{2+} ions were consumed by the precipitation than released from the composite, leading to the decrease of Ca concentration in the SBF over extended period of time. The constant decrease in P concentration over time indicated that after initial release of the P ions into the solution,

the precipitation rate of the P ions was higher than the release rate during extended period of immersion of the samples.

The CaCO_3 detected in the precipitate at the early stage of T10HAT immersion was caused by excessive Ca^{2+} ions released from the composite. In addition to forming apatite with HPO_4^{2-} , the Ca^{2+} ions near the surface could react with the HCO_3^- in the SBF to form CaCO_3 [45]:

The formation of CaCO_3 reduced the HCO_3^- concentration in the solution and the deposited CaCO_3 inhibited release of Ca from the composite by covering the surface, which can also contribute to the slowing down of the Ca^{2+} release into the SBF solution. Due to the fact that the HCO_3^- concentration in human plasma is more than 6 times higher than that in the SBF, higher concentration of CaCO_3 is expected to form after *in vivo* implantation [45].

5 Conclusions

An innovative cladding method was developed to join the Ti/HA composites to the Ti6Al4V substrate. With the application of a silver interlayer and an external pressure during sintering, the Ti/HA composites were seamlessly bonded to the substrate. After soaking in the SBF for a short time, the fabricated materials could induce the nucleation and formation of the carbonated apatite. The *in vitro* test demonstrated that the cladding process provides bioactivity and also introduced the antibacterial function of Ag to the material. Therefore, the described cladding process provides a promising route to

promote the bioactivity of Ti alloys with antibacterial function for load-bearing implant applications.

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

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	HPO ₄ ²⁻	SO ₄ ²⁻
Kokubo's SBF	142.0	5.0	2.5	1.5	147.8	4.2	1.0	0.5
Blood plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5

Fig. 1 SEM micrographs of the cross section of the specimen after sintering

(a) T5HAT; (b) T10HAT;

Fig. 2 Elemental distributions in T5HAT near the interface mapped by EDX: (a)

micrograph of the site; (b) Ti; (c) Al; (d) Ag; (e) P; (f) Ca

Fig. 3 XRD patterns of T5HAT and Ti10HAT after sintering

Fig. 4 XPS survey spectra of the composite surfaces

Fig. 5 The high resolution XPS spectra of the elements on the composite surfaces and the corresponding deconvolution: (a1-a4) T5HAT; (b1-b4) T10HAT

Fig. 6 SEM morphologies of T5HAT before and after immersion in the SBF for various times: (a) before immersion; (b) 8h; (c) 1day; (d) 3days; (e) 1week; (f) 2 weeks

Fig. 7 SEM morphologies of T10HAT before and after immersion in the SBF for various times: (a) before immersion; (b) 8h; (c) 1day; (d) 3days; (e) 1 week;(f) 2 weeks

Fig. 8 XRD patterns of the precipitated layers on the composite surface after soaking in SBF for various times: (a) T5HAT; (b) T10HAT; (T: Ti; A: apatite; C: CaCO_3)

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

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