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Corrosion Behaviour of Selective Laser Melted Ti-TiB Biocomposite in Simulated Body Fluid

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Abstract: The corrosion behaviour of CP-Ti and Ti-TiB composite produced by selective laser melting (SLM) in the artificial simulated body fluid (Hank's solution) at body temperature, was investigated systematically by using electrochemical measurements (potentiodynamic polarisation curves and electrochemical impedance spectroscopy), together with some detailed structural characterisations. The results demonstrate that SLM-produced Ti-TiB composite samples possess better corrosion resistance than SLM-produced CP-Ti samples in Hank's solution. Due to these tiny TiB and TiB₂ particles acting as the micro-cathode uniformly distributing in titanium matrix, anodic dissolution of titanium matrix in the corrosion process is prominently facilitated in early stages, followed by rapid passivation on the surface. The corrosion mechanism of Ti-TiB composite samples has also been discussed in detail at the end of this paper.

Keywords: Titanium biocomposite; Selective laser melting; Corrosion resistance; Passive film.

1. Introduction

Commercially pure titanium (CP-Ti) has been routinely employed in the area of biomedical treatment over the last 40 years or so [1-3]. This revolutionary application was triggered due to the perceived biocompatibility and appropriate mechanical properties of CP-Ti [4-6], which does not cause allergy and produce human pollutants when it is used as artificial scaffold, hip joint and dental implants [7-9]. In addition, the corrosion resistance of CP-Ti material is far superior to the other metallic materials, such as stainless steels and cobalt-chromium based composite materials [10, 11], because of the spontaneous formation of a dense and chemically stable titanium film, mainly TiO_2 , on the surface of CP-Ti [12-14]. Nevertheless, CP-Ti is beset by some inherent issues resulting from unfavorable properties including low hardness, poor wear resistance and inadequate specific stiffness [15, 16], which limit its long-term applications in the biomedical field, especially when artificial load-bearing implants with high wear resistance and high strength are urgently required. Therefore, it is essential that some effective measures should be taken to overcome the abovementioned drawbacks. For this purpose, some appropriate reinforcements can be embedded into the titanium matrix as needed, such as TiC, SiC, CrB and TiB_2 [17, 18]. Amongst those reinforcements, TiB_2 is the most suitable choice for its high hardness, thermodynamic stability and elastic modulus [19]. Additionally, from a medical point of view, as a biocompatible element, boron is favourable for applications of titanium materials [20, 21].

The additive manufacturing (AM) technique, also commonly known as 3D

printing, has rapidly developed throughout the past few years. Compared to the conventional powder metallurgy techniques, the AM technique has the capability of less processing procedures, shorter production cycles and lower material costs [22, 23]. Components and parts with extremely complex geometries that are difficult or impossible to be manufactured by traditional method can be easily realized with this new high-tech innovation [24, 25]. As one of the promising AM techniques, selective laser melting (SLM) has been reported to have capability of producing many high-density and high-precision metal parts [26-28]. In general, the SLM technique has some overwhelming advantages, namely producing near-full density metallic components, having a high material utilisation rate, and requiring no machining tools [29, 30]. According to the latest reports, the applications of SLM technique are now involved in simulating clinical teaching, assisting physician training, and maintaining medical devices [24, 31]. Consequently, the SLM technique stands for the new trend of the biomedical material applications in the future.

As for the titanium matrix composite material processed by SLM, their applications have gradually walked into all the aspects of industrial production. Extensive literature has reported these applications, such as transmission gear, circuit element and airplane tail [29, 32]. More importantly, SLM-produced Ti-TiB composite material, due to these striking features, could be considered as one of the most suitable candidates for high-strength and anti-wear biomedical applications [33]. Additionally, the porous structure of SLM-produced Ti-TiB composite material is conducive to bone cell growth, and can also reduce the risk of the replacement

components being rejected in patients [18, 34]. Even so, it is still unclear whether the service life of Ti-TiB composite material acting as biomedical materials can be drastically extended in comparison to that of the original CP-Ti in very aggressive environments, such as human body fluid or other solution media. With the increasing concerns of this urgent problem, it is worth exploring the corrosion behavior of Ti-TiB composite material in artificial simulated body fluid system.

In this work, the main objective is to systematically investigate the corrosion behaviour of SLM-produced CP-Ti and Ti-TiB composite material. Electrochemical measurements were performed for two types of samples in naturally aerated Hank's solution at body temperature, including potentiodynamic polarisation curves and electrochemical impedance spectroscopy (EIS). Moreover, some characterisation methods were carried out to strengthen the understanding of the corrosion mechanism of two types of samples.

2. Experimental

2.1 Sample and solution preparation

Cylindrical samples of CP-Ti and Ti-TiB (4 mm in diameter and 10 mm in height) produced by selective laser melting (SLM) were used in this work. Prior to SLM processing, spherical titanium powder (99.7% purity, average particle size (d) = 48.69 μm) was mixed with the prepared irregular-sharped TiB_2 particles (98.9% purity, average particle size (d) = 3.5 - 6 μm) to form Ti-5wt.% TiB_2 mixture. The ball milling method was utilised to grind the Ti-TiB₂ mixture using a Retsch planetary ball

mill under a high-purity argon atmosphere. In order to make the TiB_2 particles uniformly dispersed around the titanium matrix and thus desirable for SLM, it is necessary to ensure a milling time of 2 hours, until the Ti- TiB_2 mixture almost keep in an utmost spherical morphology [19, 35]. In the SLM process, these samples were manufactured by a MTT SLM 250 HL machine containing a 400 W Yb: YAG fiber laser with an 80 μm spot size. The samples were produced under a laser power of 180 W, a laser scanning speed of 150 mm/s, a 100 μm hatching distance and a 100 μm layer thickness. The direction of scanning was rotated through 90 degrees between each layer [19, 36].

Prior to the tests, all the cylindrical samples were connected with copper wire by solder and sealed with epoxy resin. Then, the surface of all samples were mechanically ground up to 3000 grit by SiC abrasive paper, and polished with suspension containing diamond powder [37]. Additionally, all samples were ultrasonically degreased with acetone for 5 minutes, rinsed in double-distilled water for 3 minutes, and dried in a desiccator for 12 hours in sequence. These as-treated samples were prepared for the electrochemical measurement and surface characterizations.

All electrochemical tests were carried out in aerated artificial simulated body fluid (Hank's solution) at body temperature (37 ± 0.2 °C); the pH value of Hank's solution was adjusted to 7.4 (normal pH value of human body fluid lies between 7.35 and 7.45). The compositions of Hank's solution (Model H9269, Sigma-Aldrich, USA) are listed in Table 1. Table 2 shows a comparison of the inorganic ions of Hank's

solution and blood plasma, which suggests that the components and content of Hank's solution were similar to the body blood plasma. In order to observe the metallurgical microstructure characteristics of the samples, a Kroll's solution composed of 5% HF, 10% HNO₃ and 85% double-distilled water (volume fractions) was used as etching solution, prepared using laboratory analytical grade chemicals and double-distilled water [18, 38].

2.2 Electrochemical measurements

Electrochemical measurements were carried out at body temperature using a beaker containing 350 ml naturally aerated Hank's solution, with an electrochemical workstation (Reference 1000, Gamry, USA). The device with a conventional three-electrode cell (ASTM: G3-89) consists of ~3 cm² platinum sheet as the counter electrode, these polished samples as working electrode with an exposed area of 0.13 cm², and a saturated calomel electrode (SCE) as reference electrode connected to a Luggin capillary bridge. An electro-thermostatic water bath was used to maintain a constant temperature. The potentiodynamic polarisation curves of SLM-produced CP-Ti and Ti-TiB samples were recorded and monitored from -0.5 V to 1.6 V versus the open circuit potential (OCP), with a sweep scan rate of 0.1667 mV/s. Meanwhile, the electrochemical impedance spectroscopy (EIS) data acquisition was performed at OCP potentiostatically, by scanning a frequency range from 10⁻² Hz to 10⁵ Hz with voltage perturbation amplitude of 10 mV. All potentials mentioned in this work were measured with respect to saturated calomel electrode (SCE).

2.3 Characterisation

The phase characterization of the polished SLM-produced CP-Ti and Ti-TiB samples were measured by X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA. The diffraction angle (2θ) ranged from 30° to 80° with the step size of 0.02° and a counting time of 5 seconds per step. The software Jade 6.5 was used to identify the different phases of two types of samples.

Metallographic microstructure characterisations were carried out on the polished and etched (prepared Kroll's reagent) SLM-produced CP-Ti and Ti-TiB samples by using optical microscope (LSM-510, Carl ZEISS, Germany). The microstructure of the as-polished samples and morphology after potentiodynamic polarisation and immersing in Hank's solution for 7 weeks at body temperature were characterised by a field emission scanning electron microscopy (FE-SEM, JSM-7800F, JEOL, Japan) equipped with energy dispersive spectrometry (EDS, Oxford Instruments).

Because of the existence of corrosion effect after long-term implantations, the corrosion products or titanium ions could transport into the body fluid, which may produce inside pollutants, thereby causing chronic inflammation and even incurring serious bacterial infection around the implants [6, 14]. Therefore, it is necessary to study the corrosion behaviour of CP-Ti and Ti-TiB biomaterials in the human body. Furthermore, ultraviolet-visible (UV-VIS) absorption spectra of Hank's solution were obtained after different immersion time (i.e. 1, 2, 3, 4, 5, 6, and 7 weeks) of two types of samples at body temperature, by using UV-VIS spectrophotometry (UV-2550,

Shimadzu, Japan). The spectrum of Hank's solution that had no contact with samples acted as reference, and double-distilled water was used as blank. The spectra were measured ranging from 200 nm to 400 nm [7].

3. Results

3.1 Electrochemical measurements

Fig. 1 illustrates the typical potentiodynamic polarisation curves of the SLM-produced CP-Ti and Ti-TiB samples in aerated Hank's solution at body temperature. Two types of samples both exhibit good repeatability. Table 3 shows some parameters acquired from the polarisation curves, such as passive region range (ΔE), passivation current density (j_p) and breakdown potential (E_b). It is observed that a typical passive region is present in the curves for both CP-Ti and Ti-TiB samples. Specifically, Ti-TiB samples have a relatively broader passive region (0.40 V - 1.25 V) in comparison with CP-Ti samples (0.40 V - 0.70 V). With regard to passivation current density (j_p), the average value for Ti-TiB samples was approximately $0.22 \mu\text{A cm}^{-2}$, which is considerably far below that of CP-Ti samples ($0.75 \mu\text{A cm}^{-2}$). As a general rule, j_p represents the passivation current for the film formed on the metal surface, and a small value of j_p normally means easy passivation of the samples [39]. Additionally, as another important corrosion parameter, the breakdown potential (E_b) is usually employed to evaluate the susceptibility of the passive film to damage by halide ions. As for the breakdown potential (E_b), a greater value of the E_b indicates the more stable passive film formed on the metal surface [23]. As a result, Ti-TiB samples

have a greater value of E_b compared to CP-Ti samples, which suggests that SLM-produced Ti-TiB samples have better corrosion resistance compared with SLM-produced CP-Ti samples.

The Fig. 1 inset shows the segmental magnification of the polarisation curves of SLM-produced CP-Ti samples. This suggests that the CP-Ti samples exhibit active-passive behaviour during the anode polarisation process when the potential ranges from 0.15 V to 0.35 V, which indicates incomplete passive behaviour at OCP [40]. Afterward, CP-Ti samples show stable passive behaviour with increasing potential. In this segmental anode polarisation progress, CP-Ti samples could generate a large number of Ti^{4+} in the first step, because of the presence of Cl^- [41]. The released Ti^{4+} then transport into the electrolyte and react with the substances (e.g., Cl^-) of the Hank's solution [9]. Finally, the previously formed $[\text{TiCl}_6]^{2-}$ complex would be hydrolyzed when the concentration of the $[\text{TiCl}_6]^{2-}$ complex reaches a critical value, and the TiO_2 passive film subsequently formed on the metal-electrolyte surface, which prevents the interaction between the Ti matrix and the corrosive medium and thereby decreasing corrosion tendency (Eq.1) [9, 42]:

Nevertheless, SLM-produced Ti-TiB samples do not show such a similar behaviour in the anode polarisation, but directly enter into the passive region, which verifies the easy passivation mentioned above.

Fig. 2 shows the SEM images of two types of samples after potentiodynamic polarization experiments. For SLM-produced CP-Ti samples (Fig. 2(a)), many pits

and massive corrosion products can be observed across the surface, and the size of these pits ranges from nano-scale to micron-scale. In contrast, as seen in Fig. 2(b), this scenario doesn't occur in the SLM-produced Ti-TiB samples. Instead, the surface of the SLM-produced Ti-TiB samples is covered with TiO_2 passive film (grey), which effectively inhibits Cl^- ions from eroding the titanium matrix.

Figs. 3(a) - (c) display the representative Nyquist and Bode plots for the SLM-produced CP-Ti and Ti-TiB samples in aerated Hank's solution at body temperature. From the Nyquist plot (Fig. 3a), it is clearly observed that only a big single capacitive arc is visible for both samples. However, the Bode plots (Fig. 3(c)) show a plateau from intermediate frequencies to low frequencies. Therefore, in Fig. 3(d), an equivalent circuit comprised of two time constants was used to simulate the corrosion behaviour, in order to better fit the EIS data of CP-Ti and Ti-TiB samples. In this equivalent circuit, R_s corresponds to the solution resistance; R_f describes the resistance of the passive film formed on the metal surface; R_{ct} reflects the charge transfer resistance; and CPE_1 and CPE_2 are constant phase elements, representing the deviation from ideal capacitive behavior of the passive film and double-layer, respectively, which can be ascribed to roughness or defects of the electrode surface [42, 43].

Table 4 lists the fitting results of the EIS measurements. Chi-square values (χ^2) between 2.4×10^{-3} and 9.2×10^{-3} suggest good quality of fitting these obtained EIS data. The fitting results show that the average value of R_f of SLM-produced Ti-TiB samples ($2.05 \text{ M}\Omega \text{ cm}^2$) is considerably greater than that of SLM-produced CP-Ti samples

(0.31 MΩ cm²). Normally, a higher value of R_f means better corrosion resistance of samples [4]. The greater average value of R_{ct} of SLM-produced Ti-TiB samples (1.44 MΩ cm²) in comparison with SLM-produced CP-Ti samples (0.54 MΩ cm²) has also supported this conclusion.

3.2 Structure and surface characterisation

Fig. 4 presents XRD patterns of the SLM-produced CP-Ti and Ti-TiB samples. Only hexagonal close packed (hcp) α -Ti is present in the CP-Ti sample, i.e., (100) _{α -Ti}, (002) _{α -Ti}, (101) _{α -Ti}, (102) _{α -Ti}, (110) _{α -Ti}, (103) _{α -Ti}, (200) _{α -Ti}, (112) _{α -Ti}, (201) _{α -Ti}. Similarly, the main diffraction peaks of the SLM-produced Ti-TiB sample can also be indexed as the aforementioned hcp α -Ti. In addition, some minor diffraction peaks in the pattern correspond to α phase with TiB, i.e., (102) _{α -TiB}, (210) _{α -TiB}, (020) _{α -TiB}. Combined with the results from the previous reports [15, 36], it is reasonable to suggest that the formation of TiB results from the reaction between the titanium matrix and TiB₂ particles during the SLM processing, which explains the presence of TiB and the lack of diffraction peaks for TiB₂ in the XRD patterns (Fig. 4).

Figs. 5 shows the optical micrographs of SLM-produced CP-Ti and Ti-TiB samples. As depicted from Fig. 5(a), the microstructure of CP-Ti consists of blocky primary α -Ti (bright color) and many coarse α -Ti grains (dark color). For these coarse grains, they are the dendritic phases that were generated in the SLM process. The average sizes of these coarse α -Ti grains are 2 μ m in width and 16 μ m in length. Nevertheless, compared to SLM-produced CP-Ti samples, SLM-produced Ti-TiB samples exhibit different microstructural feature. The coarse α -Ti grains have been

obviously refined into many ultrafine grains (bright color) and the measured average sizes are 0.5 μm in width and 1.0 μm in length, as shown in Fig. 5(b). As such, the SLM-produced Ti-TiB samples show far finer α -Ti grains compared with SLM-produced CP-Ti samples. Actually, the addition of the TiB_2 particles may suppress the further growth of α -Ti grains. Based on previous reports [19, 44], the grain refinement of α -Ti grains in SLM-produced Ti-TiB composite could be attributed to the boron element addition.

As seen from Fig. 6(a), some dark-coloured areas with size of 3 - 4 μm (e.g., area A) and some smaller dark-coloured areas with size of 1-1.5 μm (e.g., area B) are distributed in the titanium matrix. Figs. 6(b) and (c) show EDS results of area A and area B, respectively. According to the atomic ratio analysis from EDS results, area A is titanium diboride (TiB_2) and area B is titanium monoboride (TiB). The tests on other dark-coloured areas show the same EDS analysis results. Therefore, it can be concluded that the large dark-coloured areas that like area A are residually unreacted titanium diboride (TiB_2) reinforcement and that the relatively smaller areas analogous to area B are titanium monoboride (TiB) products. Incidentally, the absence of titanium diboride (TiB_2) from the XRD patterns in Fig. 4 could be ascribed to its low volume fraction in the samples.

Figs. 7(a) - (g) show the ultraviolet absorption spectra of Hank's solution after different immersion time for SLM-produced CP-Ti and Ti-TiB samples at body temperature. It is evident that there exists an absorption peak at maximum absorbance peak of $\lambda = 275 \text{ nm}$ in all absorption spectra, except for the reference solution. Alves

et al. [7] have confirmed that the absorption peak is related to some soluble substance of titanium (e.g., $[\text{TiCl}_6]^{2-}$) from the CP-Ti and Ti-TiB samples. For our cases shown in Fig. 7, all absorption peaks corresponding to SLM-produced CP-Ti samples are more intense than those for SLM-produced Ti-TiB samples at every testing period, which indicates higher concentration of the soluble $[\text{TiCl}_6]^{2-}$ complex from CP-Ti samples than from Ti-TiB composite samples.

Fig. 7(h) displays the relationships between the intensity of ultraviolet absorption and the immersion time. Obviously, it can be seen that both the two polylines have a similar tendency; the intensity of ultraviolet absorption increases linearly with the increasing immersion time during the first three weeks, because of the relatively rapid corrosion of titanium matrix from SLM-produced CP-Ti and Ti-TiB samples. Over immersion time, ultraviolet absorption has a slight downward trend and remains in a stable state in the end, implying that a dynamic balance is reached between the dissolution of titanium matrix and the formation of a TiO_2 film for SLM-produced CP-Ti and Ti-TiB samples during the experimental stage. This completely corroborates the results of the aforementioned electrochemical measurements.

Fig. 8 displays the SEM images of SLM-produced CP-Ti and Ti-TiB samples after immersing in Hank's solution for 7 weeks at body temperature. Obviously, there exist same corrosion products for both samples. Fig. 8(b) shows the entire process of these corrosion products from a ball-like product to gathered chunks. Some previous studies have interpreted that these titanium corrosion products could give Cl^- the access to damage the TiO_2 passive film and even induce pitting to occur on the

titanium substrate [45, 46]. In Figs. 8(a) and (c), more corrosion products for SLM-produced CP-Ti samples in comparison to Ti-TiB samples indicate that SLM-produced CP-Ti is more susceptible to be corroded than SLM-produced Ti-TiB composite.

4. Discussion

The passivation mechanism about titanium and titanium matrix composites has been discussed in recent years. There is a consensus that its passive behaviour embodies the dissolution-precipitation mechanism [47, 48]. That is, dissolution of titanium matrix takes place almost simultaneously as the establishment of the TiO_2 film in the passivation process. Previous studies suggest that the presence of substantial Cl^- results in the corrosion of titanium to form $[\text{TiCl}_6]^{2-}$ complex and that these chlorocomplex benefits for the passive behaviour of titanium matrix materials [49]. In particular, the passive film would form only if the concentration of $[\text{TiCl}_6]^{2-}$ complex reaches a critical value. Herein, the addition of TiB_2 reinforcement into the titanium matrix facilitates dissolution in the early corrosion stage, which provides favourable conditions for forming passive film. As seen from the schematic illustration of corrosion process for SLM-produced Ti-TiB composite samples (Fig. 9), a small amount of TiB products and unreacted TiB_2 particles are distributed around the titanium matrix. The dispersion of these electrical conductors (TiB_x particles) in the titanium matrix result in the formation of numerous galvanic couples; these particles act as micro-cathode and titanium matrix act as anode [50, 51]. More

specifically, the establishment of these galvanic couples further accelerates the dissolution of titanium in the early stages, which makes the concentration of $[\text{TiCl}_6]^{2-}$ complex reach a critical value, thereby rapidly forming a stable passive film to prevent the titanium matrix from being eroded. Furthermore, this conclusion is strongly confirmed by the greater value of R_f for the SLM-produced Ti-TiB composite samples (Fig. 3 and Table 4). Then the comparison of passive behaviour for two types of samples (Fig. 1), namely smaller passivation current density (j_p), wider passive region range (ΔE) and higher breakdown potential (E_b) for Ti-TiB samples, demonstrates that SLM-produced Ti-TiB composite samples have better passivation capability than SLM-produced CP-Ti samples. It has been reported that titanium and titanium matrix materials having better passivation capability commonly show superior corrosion resistance in corrosive systems [39]. In addition, ultraviolet absorption spectra (Fig. 7) have demonstrated that the dissolution of titanium matrix for CP-Ti sample is more violent than that of Ti-TiB sample over a long immersion time, which implies that SLM-produced Ti-TiB composite sample is more resistant to corrosion in Hank's solution.

Moreover, some studies have shown that grain refinement could have an important impact on the corrosion resistance of titanium and titanium matrix composites [52, 53]; and that ultrafine particles of metallic materials could greatly decrease fluctuation of the passive film and strengthen its stability [54, 55]. In this study, metallographic micrographs (Fig. 5) show that the addition of TiB_2 particles refine the coarse α -Ti grains in SLM-produced Ti-TiB composite. Thus, the protection

property and stability of the passive film on the surface of SLM-produced Ti-TiB composite samples are better than those of SLM-produced CP-Ti samples.

5. Conclusions

Both electrochemical performance and ultraviolet absorption spectrum analyses suggest that SLM-produced Ti-TiB composite samples have better corrosion resistance than SLM-produced CP-Ti samples. These TiB₂ and TiB particles act as micro-cathode and the titanium matrix acts as anode during corrosion process in simulated body fluid (Hank's solution) at body temperature. Anodic dissolution of titanium matrix in the corrosion process is facilitated, which accelerates the formation of the protective film on the surface of Ti-TiB composite samples. Above all, TiB₂ reinforcement added into titanium matrix benefits for improving the resistance of the titanium metal against corrosion.

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Figures

Fig. 1. The polarisation curves of CP-Ti and Ti-TiB samples produced by SLM immersed in aerated Hank's solution at body temperature.

Fig. 2. SEM images of (a) SLM-produced CP-Ti samples and (b) SLM-produced Ti-TiB composite samples after polarisation tests in aerated Hank's solution at body temperature.

Fig. 3. Electrochemical impedance spectroscopy for CP-Ti and Ti-TiB samples produced by SLM immersed in aerated Hank's solution at body temperature: (a) Nyquist plots (b) and (c) Bode plots

and (d) equivalent circuit model.

Fig. 4. XRD patterns of CP-Ti and Ti-TiB samples produced by SLM.

Fig. 5. Optical micrographs of (a) SLM-produced CP-Ti samples and (b) SLM-produced Ti-TiB composite samples.

Fig. 6. SEM image of (a) the polished SLM-produced Ti-TiB composite samples with Ti matrix surrounding TiB_2 and TiB particles and the EDS spectra of area A (b) and area B (c).

Fig. 7. UV absorption spectra of Hank's solution after different immersion time for CP-Ti and Ti-TiB samples produced by SLM, at body temperature (a-g); Relationship between intensity of UV absorption and immersion time (h).

Fig. 8. SEM images of samples after immersing in Hank's solution for 7 weeks at body temperature for (a) and (b) SLM-produced CP-Ti samples, (c) and (d) SLM-produced Ti-TiB composite samples.

Fig. 9. Schematic illustration of corrosion process for SLM-produced Ti-TiB composite samples. In this process, these TiB_x act as anode and form galvanic couples with their surrounding titanium.

The formation of the galvanic couples prominently facilitates anodic dissolution of titanium matrix in the corrosion process and followed by rapid passivation on the surface.

Table 1.

Chemical composition (in wt. %) of Hank's solution.

Reagent	Composition (g/L)	Reagent	Composition (g/L)
NaCl	8.00	KCl	0.40
NaHCO ₃	0.35	CaCl ₂	0.15
MgCl ₂ ·6H ₂ O	0.10	KH ₂ PO ₄	0.06
Na ₂ HPO ₄	0.06	MgSO ₄ ·7H ₂ O	0.06
D-Glucose	1.00		

Table 2.

Concentration of inorganic ions (mmol/L) of Hank's solution and blood plasma.

Ions	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	H ₂ PO ₄ ⁻ / HPO ₄ ²⁻
Hank's	142.9	5.8	0.6	1.5	144.2	4.2	0.2	0.9
Blood	142.0	4.3	1.1	2.5	104.0	24.0	1.0	2.0

Table 3.

Corrosion parameters obtained from polarisation curves of CP-Ti and Ti-TiB samples produced by SLM immersed in aerated Hank's solution at body temperature.

Sample	$j_p / \mu\text{A cm}^{-2}$	$E_b / \text{V (vs. SCE)}$	$\Delta E / \text{V (vs. SCE)}$
CP-Ti	0.74	0.70	0.30
	0.71	0.71	0.30
	0.79	0.69	0.29
Average value	0.75	0.70	0.30
Std Dev	0.04	0.01	0.01
Ti-TiB	0.25	1.20	0.78
	0.16	1.25	0.80
	0.22	1.23	0.78
Average value	0.22	1.23	0.79
Std Dev	0.05	0.03	0.01

Table 4

Fitting results of EIS for the CP-Ti and Ti-TiB samples produced by SLM immersed in aerated Hank's solution at body temperature.

Sample	R_f ($M\Omega\text{ cm}^2$)	$CPE_1 \times 10^{-6}$ ($\Omega^{-1}\text{ cm}^{-2}\text{ S}^{-n}$)	n_1	R_{ct} ($M\Omega\text{ cm}^2$)	$CPE_{dl} \times 10^{-6}$ ($\Omega^{-1}\text{ cm}^{-2}\text{ S}^{-n}$)	n_2	$\chi^2 \times 10^{-3}$
CP-Ti	0.31	12.91	0.88	0.47	18.65	0.84	9.2
	0.22	12.30	0.86	0.53	13.97	0.80	4.4
	0.41	11.11	0.85	0.63	18.48	0.83	7.5
Average value	0.31	12.10	0.86	0.54	17.03	0.82	7.0
Std Dev	0.10	0.01	0.02	0.08	0.01	0.02	-
Ti-TiB	1.20	3.11	0.91	1.20	5.67	0.85	7.3
	2.16	2.28	0.90	1.27	3.31	0.85	2.4
	2.79	4.64	0.88	1.86	6.45	0.87	9.1
Average value	2.05	3.34	0.90	1.44	5.14	0.86	6.3
Std Dev	0.79	0.01	0.02	0.36	0.01	0.01	-