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Preparation and bioactivity of SiO_2 functional films on titanium by PACVD

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Abstract: SiO_2 functional films were deposited on the surface of titanium by plasma assisted chemical vapour deposition(PACVD) and the composition of films was studied by XPS. Samples deposited with SiO_2 films were immersed in different concentration simulated body fluid(SBF) for biomimetic deposition of hydroxyapatite(HA). The results show that SiO_2 functional films deposited on titanium surface with PACVD have good bioactivity. Hydroxyapatite is formed while titanium coated with SiO_2 is immersed in simulated body fluid for seven days.

Key words: titanium; SiO_2 film; bioactivity; plasma assisted chemical vapour deposition; simulated body fluid

1 Introduction

Titanium alloy has high specific strength and good corrosion resistance. When hydroxyapatite is deposited on the surface of titanium alloy, it has both the advantages of metallic materials and bioactive ceramic materials, and can be used as a kind of perfect bone tissue implant materials[1−2]. Titanium alloy has no good bioactivity. When titanium alloy was planted into body directly, it is easy to form fibrous connective tissue and hard to form chemical bond combining with surrounding bone tissue[3]. SiO_2 has good bioactivity. When it is deposited on titanium, SiO_2 functional layer can improve the bioactivity of titanium markedly. At present, bioactivity and mechanism of SiO_2 films have got great attention of lots of researchers. SiO_2 films with the method of sol-gel[4] have so many influencing factors, so it is hard to control the quality. There also exist problems of preparation of $CaO-P_2O_5-SiO_2$ series bioactive glass, such as complex process and long time treatment[5−8]. TiO_2-SiO_2 films[9] prepared with sol-gel method on the surface of NiTi alloy do not exhibit perfect bioactivity. The method of PACVD of SiO_2 films is provided with advantages of low temperature, good combining interface and easy processing[10]. Bioactivity and preparation of SiO_2 films by PACVD have seldom been reported recently. In this work, SiO_2 films were deposited on titanium substrates by PACVD and the bioactivity of samples in SBF was studied.

2 Experimental

2.1 SiO_2 films deposited by PACVD

PDC-32G plasma assisted reactor was used in experiment. Schematic map of PACVD processing is shown in Fig.1. Titanium was rinsed gently with NaOH, HF and HNO_3. TEOS and air were used as precursors. Water bath temperature is 8 ℃ and reactor pressure is 5 Pa. First, dry air was introduced into the chamber at 10 mL/s and the plasma reactor was activated for 20 min. Hydrocarbons and oxides were removed[11]. Second, another air flow at 2 mL/s was used as a carrier

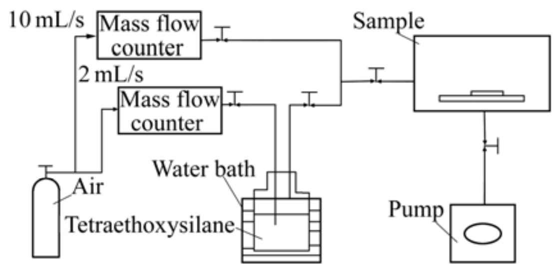

Fig.1 Schematic map of PACVD processing

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gas for transporting the TEOS vapour to plasma chamber and the deposition process was 30 min. Then, SiO_2 films with about 40 nm in thickness were obtained.

2.2 Deposition of HA in simulated body fluid

SBF with different concentrations was prepared by dissolving reagents of NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 into deionized water. The compositions of SBFs with different concentrations are listed in Table 1. Titanium pieces coated with SiO_2 films were cut into the size of 10 mm × 10 mm × 1 mm, then put into different concentration SBFs. The SBF containers were put into electric-heated thermostatic water bath for 4 d and 7 d, respectively. SBF was changed every two days. Samples were removed from SBF and rinsed gently with deionized water and analyzed by scanning electron microscopy (JSM-5610LV) and multi-technique electron spectrometer (ESCALAB MK II).

3 Results and discussion

3.1 SiO_2 functional films deposited by PACVD

Results of XPS survey spectrum of SiO_2 films deposited on titanium are shown in Fig.2. It can be seen that there exist three kinds of elements, C, O and Si. Quantitative calculation is carried out with the sensitive factor method. Quantitative data of C, O and Si are listed in Table 2.

It is shown from Table 2 that a small quantity of C (3.22%) is found in surface films. The molar ratio of O to Si in coating is 3:1, a little larger than the stoichiometric value of 2.0 for SiO_2. The increase of the x(O)/x(Si) ratio has also been observed by other researchers in silicon oxide coating. It has been explained on the basis of increased Si—O—H and Si—O—C_x—O_y types of bonds in place of Si—O—Si bonds[12].

The reaction may be written as follows:

$$SiO_4(C_2H_5)_4+12O_2 = SiO_2+10H_2O+8CO_2 \quad (1)$$

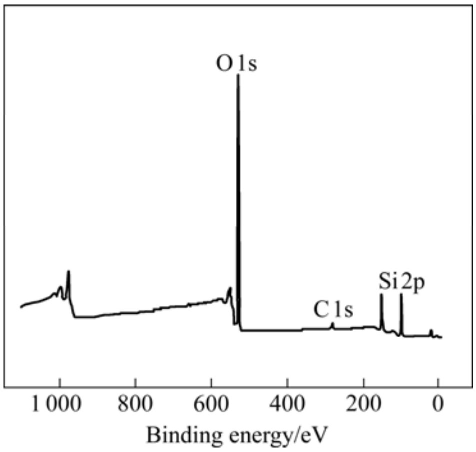

Fig.2 XPS survey spectrum of SiO_2 films

From the reaction, it is known that enough oxygen would reduce carbon content in SiO_2 functional films and more pure SiO_2 can be obtained[13].

3.2 HA deposition induced in SBF

3.2.1 Microstructure

SEM images of titanium coated with SiO_2 films immersed in No.1 SBF for 12 h and 7 d are shown in Figs.3(a) and 3(b) respectively. Fig.3(c) shows the microstructure of the sample immersed in No.2 SBF for 7 d, and Fig.3(d) shows that in No.3 SBF for 7 d. It is observed that a lot of HA has been formed when SiO_2 films are immersed in SBF for more than 12 h. It is obvious to observe that the quantity of HA increases markedly in Fig.3(b). More active sites[14−15] were supplied by noncontinuous surface, which is easy for Ca^{2+} and PO_4^{3-} to be supersaturated in some region and favorable for HA to nucleate and grow[16−17]. Flocculent (Fig.3(c)) and granular structures (Fig.3(d)) are found all over the surface. However, granular HA, with a characteristic of denseness and uniformity, almost aggregates in succession. This means that more HA is formed on the sample immersed in No.3 SBF.

Table 1 Ion concentration and composition of SBFs and human blood plasma

Sample No.	Solution	Ion concentration/(mmol·L^{-1})							
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
1	15Ca/P-SBF	142.0	5.0	37.5	1.5	103.0	27.0	15.0	0.5
2	5SBF	710.0	25.0	12.5	7.5	515.0	135.0	5.0	2.5
3	15Ca/P-5SBF	710.0	25.0	37.5	7.5	515.0	135.0	15.0	2.5
4	Human blood plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5

Table 2 Quantitative analysis results of PACVD deposition

Element	Binding energy/eV	Area/eV	Sensitive factor	Ratio of atom number	Area/%	Mass fraction/%
O 1s	530.00	170 059.10	0.66	14.29	71.45	61.36
C 1s	282.00	4 507.00	0.25	1.00	5.00	3.22
Si 2p	101.10	24 632.50	0.29	4.71	23.55	35.42

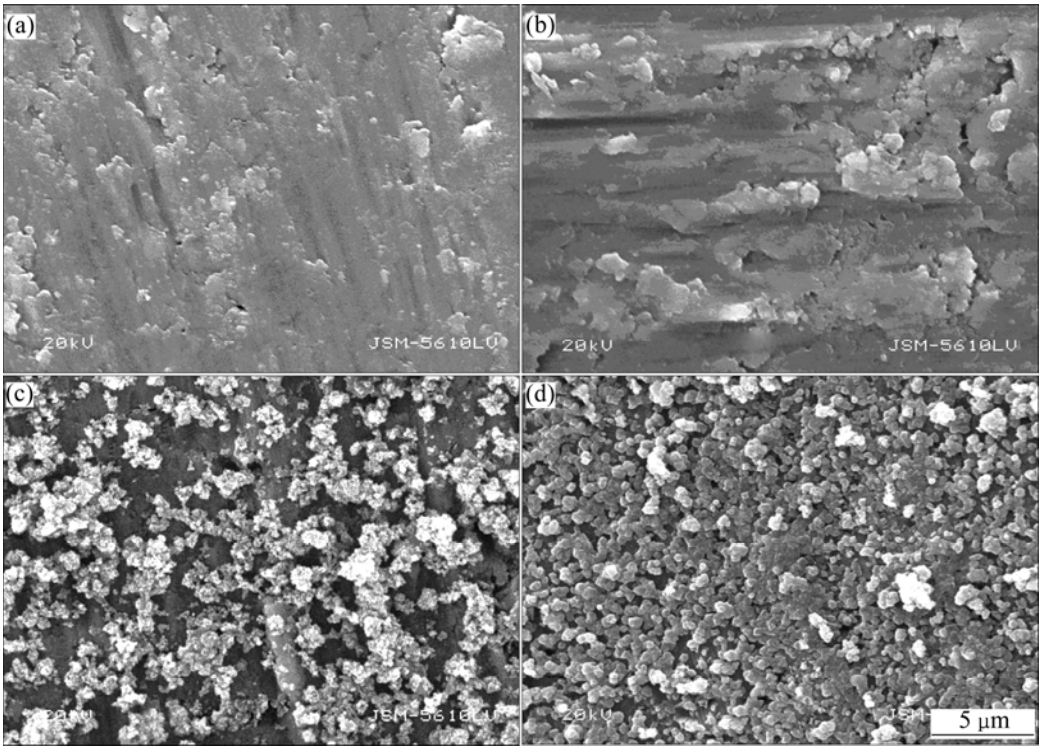

Fig.3 Microstructures of titanium coated with SiO_2 films: (a) In No.1 SBF, 12 h; (b) In No.1 SBF, 7 d; (c) In No.2 SBF, 7 d; (d) In No.3 SBF, 7 d

3.2.2 Composition of HA deposition layer

XPS survey spectrum of the sample immersed in No.1 SBF for 7 d is shown in Fig.4. Ca, P, C and O are found in the surface layer. The results show that some HA has been deposited on the SiO_2 film surface.

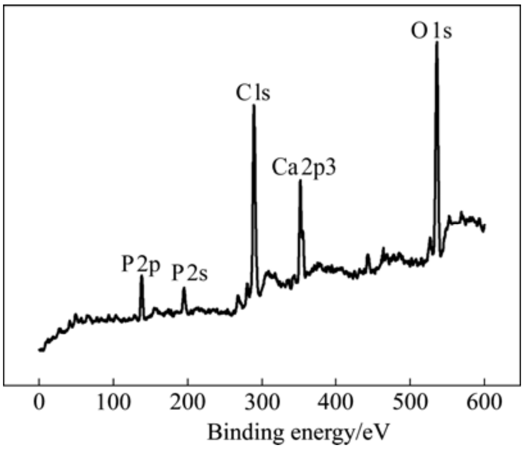

Fig.4 XPS survey spectrum of sample induced to deposit HA for 7 d

The amount of Ca, P and O elements in coating was scanned through high resolution spectra and calculated by atom sensitive factor method respectively[18−21]. The results are listed in Table 3.

It is shown from Table 3 that the molar ratio of Ca to P is 1.2:1, which is lower than that in HA. The reason is that some $CaHPO_4$ is formed in the surface layer.

Table 3 Quantitative analysis results of 7 d deposition in SBF

Element	Binding energy/ eV	Area/ eV	Sensitive factor	Ratio of atom number	Area/ %	Mass fraction/ %
Ca	347.4	22 143.3	1.58	1.2	37.5	32.9
P	133.2	4 577.3	0.39	1	7.7	21.2
O	531.5	32 366.84	0.66	4.2	54.8	45.9

3.2.3 Mechanism of HA deposition

The reaction of HA deposition is written as follows:

$$10Ca^{2+}+2OH^{-}+6PO_4^{3-}=\!=Ca_{10}(PO_4)_6(OH)_2 \qquad (2)$$

Hydrolyzation reaction of SiO_2 films can be written as follows:

$$(Si—O—Si)+H_2O=\!=Si—OH+HO—Si \qquad (3)$$

When Si—O—Si bonds break out, lots of Si—OH groups[22−23] are formed, which generates polysilicon acid, then chain and netlike structure[24] with lots of negative charge are produced.

Ca^{2+} will be adsorbed on the surface[25−27] because of much negative charge existed in Si—OH structure and the static gravitation effect. Then Ca^{2+} can adsorb HPO_4^{2-}. HA crystal nucleus forms with the increase of Ca^{2+}, PO_4^{3-} and OH^{-}. Once the crystal nucleus forms, it grows up and HA coating forms at last[4,28].

4 Conclusions

1) SiO_2 functional films, which contains small quantity of carbon, are obtained by taking the following parameters: 5 Pa chamber pressure, 8 ℃ water bath temperature, 10 mL/s air flow and 30 min plasma deposition.

2) 3.22% carbon is found in SiO_2 functional films deposited by PACVD.

3) The atomic ratio of Ca to P in the samples immersed in SBF for 7 d is 1.2:1.

4) Better HA coating can be obtained when the titanium coated with SiO_2 films is immersed in 60 ℃ 15 Ca/P-5SBF for 7 d.

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