Modeling for Calcium Phosphate Deposition on C/C Composite by Sonoelectrodeposition process

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1. Introduction

C/C composite is a promising orthopaedic porous material. It has higher strength and toughness, especially the modulus close to bone which could avoid "stress shielding" and sequential bone absorption caused by implant materials with high elastic modulus. Additionally, C/C exhibits excellent biocompatibility. However it is bioinert. In order to endow C/C with bioactivity and have other biofunctions, calcium phosphate(CP) coatings with good biocompatibility and osteoconductivity, can be applied on it[1,2].

In our previous work, a modified electrocrystalization technique(EC), named cathode sonoelectrodeposition (SED), has been put forward[1]. The experimental results showed that the homogenous, densified and improved coatings could be obtained on different carbon materials by this method, and the H_2 bubbles evolving didn't need to be precisely controlled.

In this technique, the CP coating formation on C/C is more complicated owing to the introduction of ultrasonic to the electro-crystal process. For the seeking of the dominant control factors of CP coating deposition, a simplified physical model of the procedure has been suggested, and related mathematical expressions have also been established. In addition, the identified experiments have been presented.

2. Physical model of CP coating deposition by SED technique

The comprehension of ultrasonic effect on CP deposition by cathode electrochemical method is a premise for establishing CP coating formation model. Fig 1 shows the simplified schematic diagram of the C/C cathode (represented by a), electrolyte interface layer b and solution containing the active ionic species (represented by c). When ultrasonic is applied on the electrolyte containing Ca and P elements, the main functions of ultrasonic during the procedure of CP coating formation are as follows, one is to accelerate the diffuse of ions containing Ca and P elements towards the C/C cathode, which results in the formation of diffusion layer with ionic concentration descend, and the concentration profile is showed as the curve d in Fig 1, the other is more complicate reactions occurring near the cathode, such as sono-chemical or sonoelectro-chemical reaction, electrochemical reduction reaction, CP formation reaction on C/C cathode or in electrolyte interface layer, surface graft reaction for C/C, et al[3]. On the basis of the analysis of many SEM photos and the observation of experimental phenomena, we suggested that these reactions, such as

electrochemical reduction reaction and the surface reaction of CP deposition, are dominating for the CP coating formation.

According to the above descriptions, the procedure of CP deposition on C/C cathode by SED technique consists of two steps: the first is the movement of ions containing P and Ca elements towards the C/C cathode by means of diffusion, and the second is the CP coating formation directly on C/C surface modified as result of the sonoelectrochemical reaction.
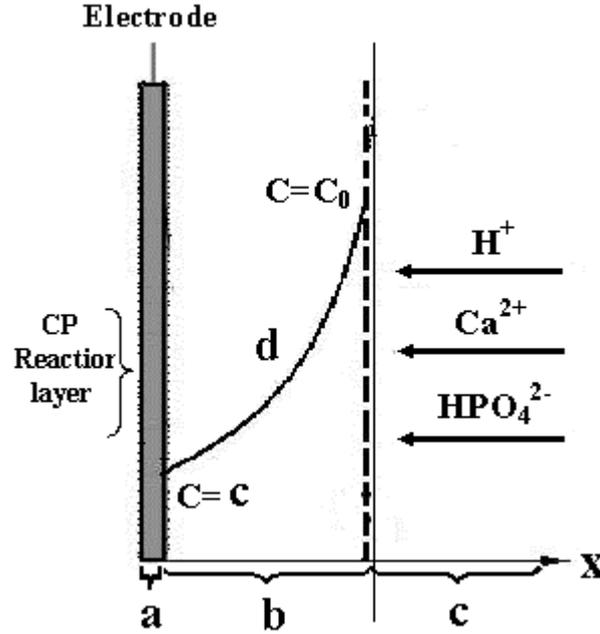
Fig 1 Schematic diagram of CP coating deposition model by SED technology

3. Mathematical describe of CP coating deposition by SED technique

Based on the above physical model, the deposited rate of CP coating consists of two parts, the rate of ion diffusion V_R and the rate of CP chemical reaction V_D[4]. According to the kinetic principle of chemical reaction and diffusion first law, they can be expressed (1) and (2) respectively:

$$V_R = KC \qquad (1)$$

$$V_D = D \left. \frac{dc}{dx} \right|_{x=s} = D \frac{C - C_0}{\delta} \qquad (2)$$

Where K is the rate constant for CP coating formation; C is ion concentration at the boundary of interface layer; C_0 is the initial concentration; D is the diffusive coefficient that is independent of concentration; δ is the thickness of diffusive layer.

When the balance is achieved for CP coating formation, the CP deposition rate will equal to the diffuse rate and CP reaction ration, i.e.

$$V = V_R = V_D \qquad (3)$$

Combining (1), (2) and (3), the following mathematical expression of CP deposited rate can be derived:

$$\frac{1}{V} = \frac{1}{KC_0} + \frac{1}{DC_0 / \delta} \qquad (4)$$

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Seen from the equation (4), it can be inferred that the CP deposition rate will be dominantly controlled by ion diffusion. If the value of DC_0/δ is much less than that of KC_0, and thus the rate V_R can be ignored, and vice versa.

Suppose that the CP deposition rate is mainly controlled by ion diffusion, Fick's second law could be introduced to describe the CP deposition procedure, the distribution of concentration is given as follows, as expected from the one-dimensional space:

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2}$$
(5)

Where t is time, C is the concentration; x is the distance of diffusion.

If no diffusion occurs before loading the electric potential, the initial condition is presented by

$$t=0, x\geq0, C(x, t)=C_0$$
(6)

If the concentration of reactants is zero on the C/C cathode surface(x=0) when loading of electric potential starts, the boundary condition is given by

$$t>0, C(0, t)=0$$
(7)

From the conditions (6) and (7), according to the solution of equation (5), the flux J (quantity per unit time per unit area) at x=0 can be given by

$$J\big|_{x=0} = D\frac{\partial c}{\partial x}\Big|_{x=0} = DC_0 \frac{2}{\sqrt{\pi}}\left(\frac{1}{2\sqrt{Dt}} e^{\frac{x}{2\sqrt{Dt}}}\right)\Big|_{x=0} = C_0\sqrt{D}/\sqrt{\pi\cdot t}$$
(8)

According to Cottrell equation and Faraday law[5], shown in equation (9) and (10) respectively:

$$i=nFAJ$$
(9)
$$i=dq/dt$$
(10)

The following expression can be gotten when x=0

$$q = nFAC_0\sqrt{D\cdot t}/(2\cdot\sqrt{\pi})$$
(11)

Where i is current, n is valence, q is total electric charge, F is Faraday's constant, and A is surface area.

Because the principle of CP coating formation by SED for C/C is alike to that of the CP deposition on titanium by EC[1], the deposited amount Am of product is directly proportional to q. thus, the ultimate expression could be presented in equation (9):

$$Am = k \cdot \sqrt{t}$$
(9)

where k is the constant that is independent of other factors.

Based on the above equation, we can deduce that if the amount Am of CP coating formation is in direct proportion to the square root of deposition time, the procedure for SED will be dominantly controlled by ion diffusion.

4. Experimental identification of the corresponding model

In order to identify the proposed models, 2D C/C specimens with the size of 10mm×10mm×1mm were used to deposit CP coating by SED at various current density 8-25mA/cm^2 or different temperature 281-343K in our CP coating deposition device

All the experimental results showed that the amount of CP formation was directly proportional to the square root of deposition time. Two examples are shown in Fig2. These results indicated the suggested models are reasonable, and the procedure of CP coating formation by SED is mainly controlled by ions diffusion in the electrolyte.
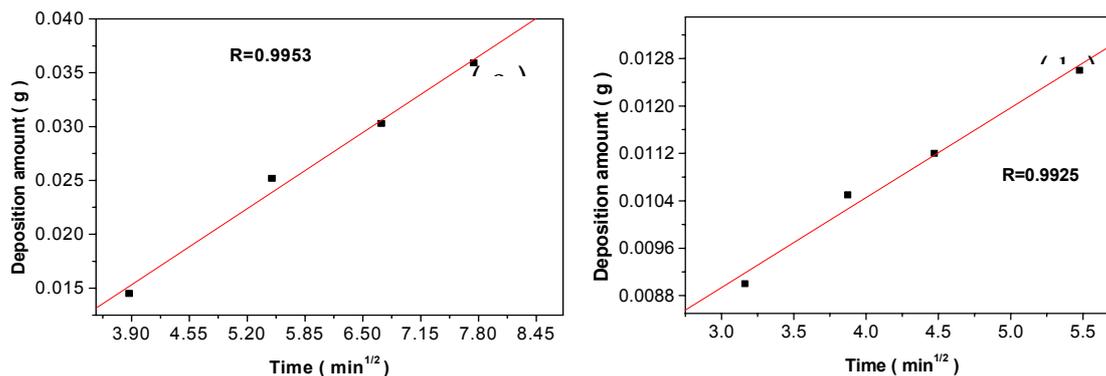

Fig2.   Relation of deposition amount and time$^{1/2}$

(a) 0.0059M 333K；(b) 0.059M 343K

5. Conclusions

To comprehend the mechanism of CP coating formation on C/C, a simplified CP deposition model has been put forward, in which the deposition procedure of CP coating consists of two steps: the first is the movement of ions containing P and Ca elements towards the C/C cathode by means of diffusion, and the second is the CP coating growth on the C/C surface. The corresponding diffuse mathematic model, related to dominant control step of the CP deposition, has also been built. The experimental results confirmed that the models are reasonable, and the procedure of CP formation for SED is mainly controlled by ions diffusion in the electrolyte.

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