Novel coating technique for preparation of hydroxyapatite/Ti composite

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Biologically active coatings have been widely used to modify metal implants, in order to endow metal materials with bioactivity and to improve interfacial strength between the implant and the host. Coatings of HA have been prepared by several techniques, for example plasma spraying [1, 2], electro-deposition [3], sol-gel method [4], laser ablation [5], and ion beam sputtering [6]. Most of these techniques involve very high temperature. The synthesis temperature of plasma spraying could be as high as 3000 °C. It is difficult to control the phase composition of coating at such a high temperature, and thermal stresses would be generated in the subsequent cooling process as well, leading to cracking and peeling of the coating [7, 8]. Recently, a new chemical coating technique has received considerable attention, involving NaOH-treatment followed by biomimetic mineralization at ambient temperature [9]. However, this coating technique has disadvantages such as long soaking time and thin coating thickness.

Combustion synthesis is another widely-used coating technique due to its low cost and convenience for controlling chemical and phase composition [10]. So far this technique has not been used for the synthesis of HA coatings. Recently, Cunyet prepared HA powder by combustion synthesis in simulated body fluid and subsequent extended annealing [11]. This method has been adopted by many other researchers in recent years, and is named as solution combustion synthesis [12]. Solution combustion synthesis is based on the combustion of an aqueous solution containing salts of the desired metals (usually nitrates) and fuel, such as urea [13], carbo-hydrazide [14], oxalic dehydrazide [15], glycine [16], etc. The combustion process is due to an exothermic redox reaction between nitrate ions and the fuel. The combustion temperature of this process is significantly lower than other coating methods. This is promising for HA coatings, since low synthesis temperature would largely decrease the thermal stress and prevent the decomposition of HA.

The present paper is devoted to preparing HA coatings by solution combustion synthesis and investigating the effect of the processing parameters on the microstructure and mechanical properties of the coating.

Ti substrates (purity: 99.8%), with a dimension of $\phi 17 \times 2$ mm^2, were treated in 1 M NaOH solution at 80 °C for 24 h, in order to form a transition layer of titanium oxides. Combustion reagents, $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$, HNO_3 (concentration of 85 vol%) and urea, were mixed in aqueous solution, and the composition is shown in Table I. In another solution, $NaNO_3$ was added in order to increase transient combustion temperature. Al_2O_3 crucibles containing the prepared solution and Ti plate were then put into a furnace at different temperatures for 15 min. After necessary surface cleaning, the coated Ti substrates underwent hydrothermal treating in an autoclave at 150 °C, 5 MPa for different times. Ammonia was added to the autoclave to adjust the pH to 12 in order to satisfy the crystallization condition of HA crystals.

The phase composition and microstructure of the coatings were analyzed by using XRD(using Rigaku-3014 and Cu K$_\alpha$ radiation) and SEM (Jeol JSM-5600LV), respectively. The interfacial bonding strength of the coatings was tested on an Instron Materials Property Tester.

XRD analysis shows that after combustion synthesis, the coatings on Ti plates were mainly composed of HA and $Ca_3(PO_4)_2$, as shown in Fig. 1. By quantitative analysis, it was found that the content of HA decreased from 47 wt% to 36 wt% when the furnance temperature increased from 500 to 600 °C. After hydrothermal treatment the HA content in the coatings increased, and pure HA coating was obtained by a 10 h treatment, shown as curve (e) in Fig. 1.

The combustion synthesis can be described as follows. When the solution containing metal salts and fuel was put into the furnace, they boiled and dried to form salt foams immediately. The fuel, for example, urea in this work decomposed into biuret, cyanuric acid, and ammonia [17, 18]. Biuret itself then decomposed above 300 °C. Nitrate salts usually decompose at temperature below 700 °C, with the evolution of gases, such as NO_2, NO, N_2O_5 [17], as described in Equation 1. $(NH_4)_2HPO_4$ also might decompose as the furnace temperature was as high as 500 °C, according to Equation 2. There gases would ignite immediately at temperature above 500 °C. This ignition was believed to increase the temperature around the dried foams instantaneously to 1300 °C [18], which would induce the reaction between the decomposed products (mostly oxides). According to Equation 3, calcium phosphates could be synthesized finally.
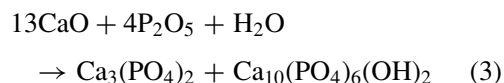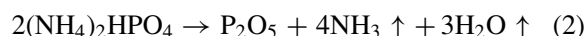
$$Ca(NO_3)_2 \rightarrow CaO + N_2O_5 \uparrow \qquad (1)$$

$$2(NH_4)_2HPO_4 \rightarrow P_2O_5 + 4NH_3 \uparrow + 3H_2O \uparrow \quad (2)$$

$$13CaO + 4P_2O_5 + H_2O$$
$$\rightarrow Ca_3(PO_4)_2 + Ca_{10}(PO_4)_6(OH)_2 \quad (3)$$

TABLE I Composition of the initial solution

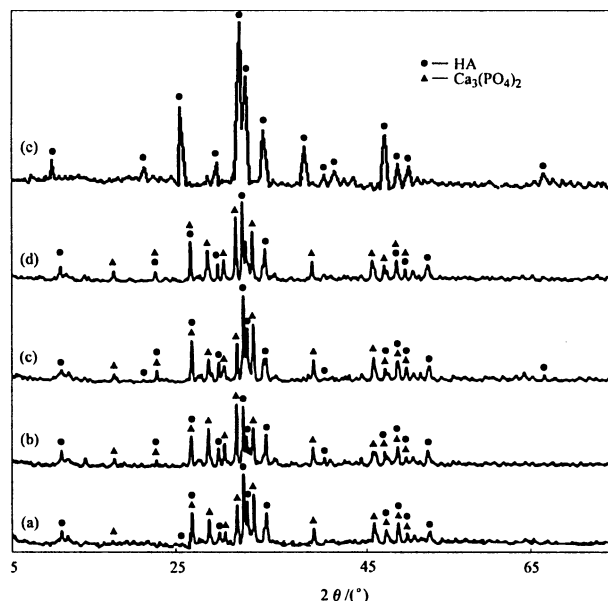| Reactants	Weight or volume
$Ca(NO_3)_2 \cdot 4H_2O$	1.457 g
$(NH_4)_2HPO_4$	0.479 g
$HNO_3(85\%)$	0.5 ml
Urea	1.83 g

Figure 1 XRD patterns of the coatings without addition of $NaNO_3$ after combustion and/or hydrothermal treatment: (a) at 500 °C, (b) at 600 °C, (c) hydrothermal treatment for 2 h at 500 °C, (d) hydrothermal treatment for 2 h at 600 °C, and (e) hydrothermal treatment for 10 h at 600 °C.

The difference between the formation of calcium phosphate powder and that of coating by solution-combustion synthesis mainly depends on the synthesis temperature. Actually, we had conducted experiments at 450 °C, but only very loose powder was obtained. Increased furnace temperature increases the local temperature around the substrate during combustion synthesis, and leads to metallurgical bonding among the reactant particles and the transition to a TiO_2 layer. However, HA is known to decompose easily at high temperature into TCP. So increasing the furnace temperature further dropped the content of HA in the coatings, as shown in Fig. 1.

With addition of $NaNO_3$, the combustion products changed to Na_3PO_4, $CaCO_3$ and some unknown phases. Pure HA coating can also be obtained after hydrothermal treatment, as shown in Fig. 2. $NaNO_3$ decomposes into oxide with the evolution of gas at a synthesis temperature of 500 °C or higher, according to Equation 4:

$$2NaNO_3 \rightarrow Na_2O + N_2O_5 \uparrow \qquad (4)$$
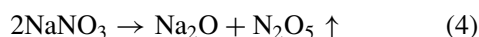
The formation of calcium phosphate was hindered by the existence of Na_2O, as the reactivity of Na_2O is higher than that of CaO, so Na_2O reacted with P_2O_5 to form Na_3PO_4 while CaO reacted with CO_2 in the furnace atmosphere to form $CaCO_3$, according to the following equations:

$$3Na_2O + P_2O_5 \rightarrow 2Na_3PO_4 \qquad (5)$$
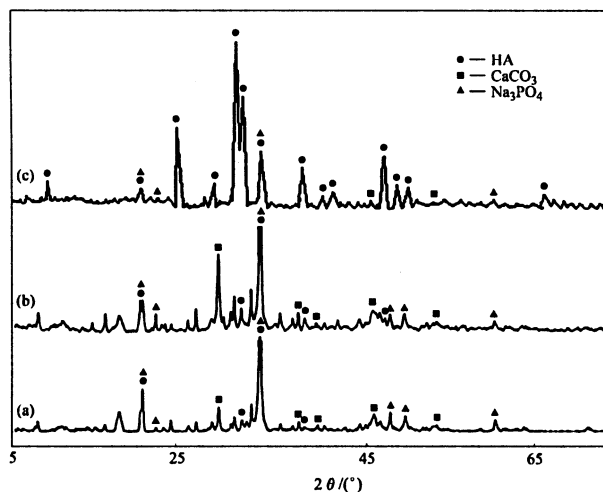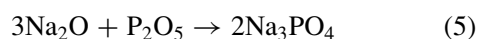
$$CaO + CO_2 \rightarrow CaCO_3 \qquad (6)$$

Figure 2 XRD patterns of the coatings with the addition of $NaNO_3$ after combustion and/or hydrothermal treatment: (a) 500 °C, (b) 600 °C and (c) 600 °C, hydrothermal treatment for 10 h.

During hydrothermal treatment, Na_3PO_4 and $CaCO_3$ reacted with ammonia in the autoclave to form HA, according to the following probable Equation 7:

$$6Na_3PO_4 + 10CaCO_3 + 2NH_3 \cdot H_2O$$
$$\rightarrow Ca_{10}(PO_4)_6(OH)_2 + 9Na_2CO_3 + (NH_4)_2CO_3$$
$$(7)$$
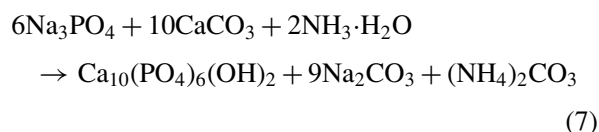
The morphology of the coatings after thermal treatment is shown in Fig. 3. As indicated in Fig. 3, the coating consisted of two layers: the transition layer and the HA coating. By means of EDX analysis, the composition of the transition layer is identified to be TiO_2. The HA crystals after solution combustion synthesis and hydrothermal treatment are rod-like, with a mean diameter of 1 μm and an aspect ratio of about 5. The addition of $NaNO_3$ increased the thickness of HA coating. For the sample without the addition of $NaNO_3$, the thickness of HA coating was measured to be about 20 μm, whereas for the sample with the $NaNO_3$, the thickness of HA coating increased to be 50 μm. Therefore, the addition of $NaNO_3$ not only changed the phase composition of the coating, but also changed the thickness of the coating. According to reaction Equation 4, N_2O_5 evolved, resulting in an increase of the reactants in the gaseous mixture and an increase in the transient combustion temperature. So the reaction products resulting from Equations 5 and 6 could be bonded together in a much denser and thicker layer.

The interfacial bonding strength of coatings is shown in Table II. It indicates that the bonding strength decreased as combustion synthesis temperature increased, and the addition of $NaNO_3$ is seen to be beneficial in improving bonding strength. The highest bonding strength in this work was obtained at a combustion synthesis temperature of 500 °C with addition of $NaNO_3$, which was lower than that of the coatings prepared by plasma spraying [1, 7]. However, the bonding strength could be further improved by subsequent heat treatment, which is still under investigation.
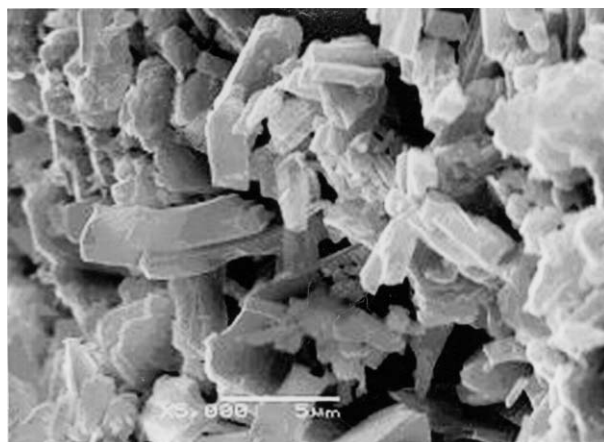
The strength of coating is highly influenced by such factors as residue stress and bonding between particles
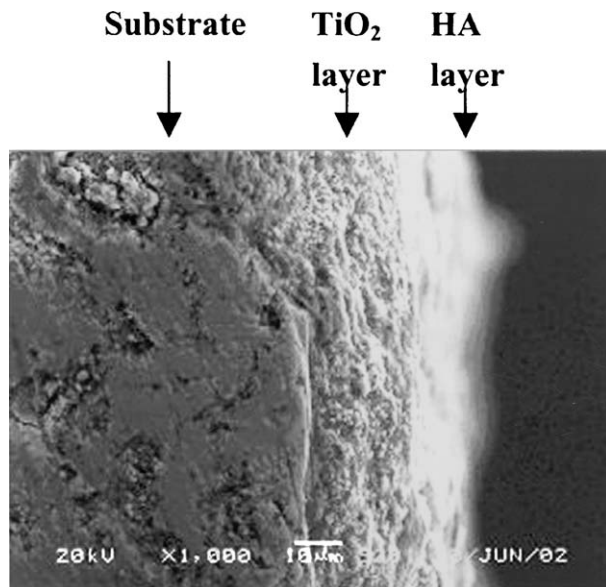
(a)
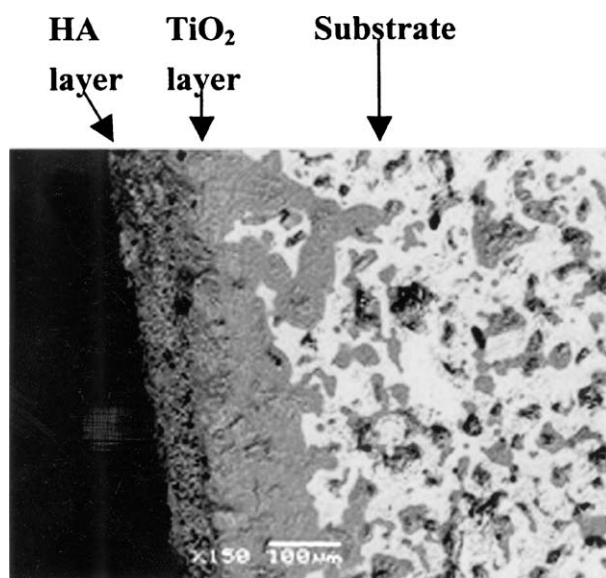
(b)

(c)

Figure 3 (a) coating without addition of NaNO$_3$, (b) coating with addition of NaNO$_3$, and (c) HA crystals in (b) after hydrothermal treatment.

TABLE II Interfacial bonding strength of the coatings

Solution	Furnace temperature (°C)	Strength (MPa)
Without NaNO$_3$	500	11.45
	600	8.81
With NaNO$_3$	500	13.66
	600	11.01

and/or different layers. There is a large difference between the thermal expansion coefficients of calcium phosphate coating, TiO$_2$ transition layer, and Ti substrate, resulting in formation of residue thermal stresses and decrease of interfacial bonding strength after cooling. Increased furnace temperature increased the thickness of TiO$_2$ transition layer from 50 μm at 500 °C to 100 μm at 600 °C, leading to larger thermal stress during cooling and decreasing the bonding strength. However, the addition of NaNO$_3$ increased the transient combustion temperature, and improved the metallurgical bonding between the coating and the TiO$_2$ transition layer, hence increasing the interfacial strength.

In conclusion, pure hydroxyapaptite coatings can be deposited on Ti substrates by solution combustion synthesis with moderate interfacial bonding strength. The composition of the combustion-synthesized coatings without the addition of NaNO$_3$ mainly consist of calcium phosphates, including β-TCP and HA, and the content of HA decreases with furnace temperature increase due to the decomposition of HA and increases with prolonged hydrothermal treatment. A Coating of pure HA can be obtained after 10 h of hydrothermal treatment. Addition of NaNO$_3$ results in improved interfacial bonding strength and coating thickness owing to the increase of instantaneous combustion temperature. However, increased furnace temperature decreases bonding strength by increasing the thickness of the oxidation layer of Ti substrate.

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