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Thermal decomposition of hydroxyapatite structure induced by titanium and its dioxide

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Titanium (Ti) implants coated with hydroxyapatite (HA), combining the ability of HA to bond with natural bone and excellent mechanical properties of titanium, have been successfully used in clinics. To improve the crystallinity of the coatings, post-heat-treatment was applied on the HA coating–titanium system. Several groups [1–4] have post-heat-treated plasma-sprayed and sputtered HA coatings, to increase their crystallinity and lower their solubility compared with the as-received coatings. Ducheyne *et al.* [5] employed a vacuum heat treatment on electrophoretically deposited HA coatings to investigate the induced changes on their structures.

Besides the benefits produced by heat treatment, there also exist some negative side-effects. Ducheyne *et al.* [5] found that the heat treated layers contain distinctively different compositions from the as-received coatings. The present authors [3] also reported that the plasma-sprayed HA coatings began to decompose at 800 °C during vacuum heat treatment.

It is well known that the HA structure is thermally stable up to 1250 °C in air [6] and to 1050 °C in vacuum [7]. So it is hypothesized that the destruction of HA structure in HA–Ti or HA–TiO_2 systems at lower temperatures than 1000 °C is completely related to the titanium and its dioxide. In the present study, HA powder was pre-heat-treated at 1200 °C for 120 min (the XRD pattern showing no decomposition) and then mechanically mixed with titanium and titanium dioxide powders. The mixtures were pressed into circular plates and sintered for 30 min in vacuum and for 60 min in air, separately, at different temperatures. The stability of the starting HA powder was also proved by heating it in vacuum ($<1.333 \times 10^{-3}$ Pa) at 1000 °C for 30 min, showing the same reflection patterns as those of the standard HA structure. The XRD patterns were determined on a RIGAKU diffractometer (D/max-γ A) with Cu-K_α radiation at 45–50 kV and 140–160 mA.

The XRD patterns in Fig. 1 exhibit phase compositions of the mixture of HA and titanium sintered at different temperatures in vacuum. The decomposition of HA induced by titanium begins at 800 °C with the appearance of traces of α tricalcium phosphate (α-TCP) and tetracalcium phosphate (TCPM). With the increase of temperature, this process becomes more extensive and no other phase is produced besides α-TCP and TCPM. The results are identical with our previous reports [3] concerning the thermal decomposition of plasma-sprayed HA coatings on titanium plates during vacuum heat treatment. No reflection corresponding to the compounds of titanium is found from XRD patterns of the sintered mixture. Therefore, we suggest that titanium catalyses the thermal decomposition of hydroxyapatite structure according to the following formula:

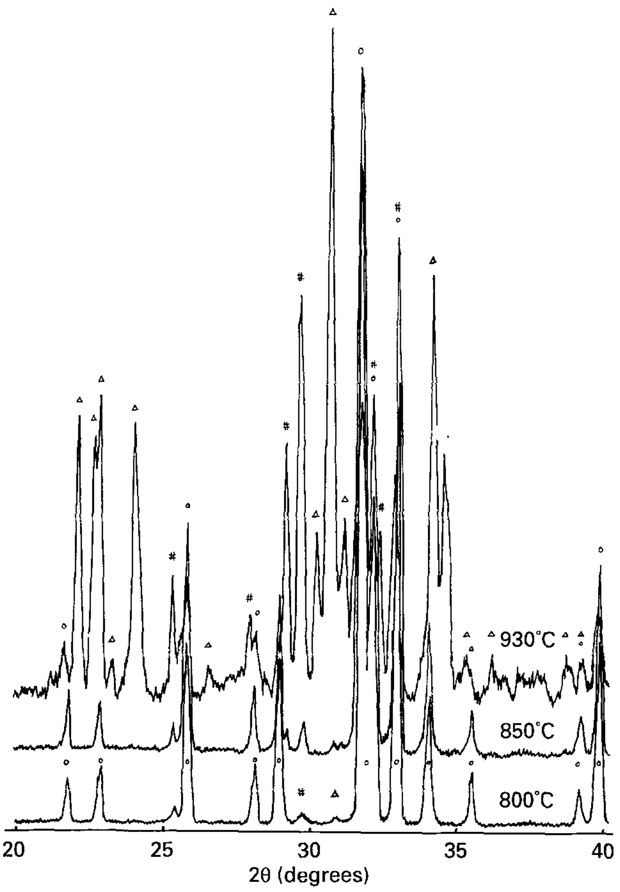

Figure 1 The XRD patterns of a HA–Ti mixtures sintered in vacuum at different temperatures for 30 min. (○ HA; △ α-TCP; # TCPM.)

$$Ca_{10}(PO_4)_6(OH)_2 \xrightarrow[\text{in vacuum}]{\geqslant 800\ ^\circ C,\ Ti} Ca_4P_2O_9 + 2Ca_3(PO_4)_2 + H_2O \quad (1)$$

Ducheyne *et al.* [15] investigated the phase transformation of electrophoretically deposited calcium phosphate ceramic (CPC) coatings on titanium substrates during vacuum sintering. Although they reported that the underlying titanium resulted in a partial transformation of HA structure to TCPM only, different from our present result, it cannot be excluded that α-TCP also existed as a resultant

0261-8028

phase (see the XRD pattern of Fig. 4(b) in [5]). Besides, in their vacuum sintering of HA + β-TCP coatings on titanium substrates, they ascribed the α-TCP phase to the transformation of β-TCP induced by the underlying titanium. According to our experimental results, it is suggested that α-TCP might also come from the decomposition of HA, while β-TCP remains approximately unchanged. In high vacuum, electron beams can destroy the HA structure and cause α-TCP to appear [8]. In the following parts of the present study, the decomposition of the HA structure, by itself at 1300 °C and induced by TiO_2 at lower temperatures, is examined and it is shown that TCP is one of the resultant phases. So it might be concluded that the decomposition of destruction of HA structure is always accompanied by appearance of TCP.

Fig. 2 shows the XRD patterns of the mixture of HA and titanium dioxide sintered in air for 60 min at different temperatures. The starting powder of titanium dioxide used here is a mixture of TiO_2 6T (rutile syn.) and TiO_2 12U (anatase syn.) HA structure starts to be destroyed at 900 °C with the formation of traces of α-TCP and calcium titanate ($CaTiO_3$). With increase of temperature higher than 900 °C, there appears β-TCP besides $CaTiO_3$ and α-TCP, and TiO_2 6T remains approximately unchanged, while TiO_2 12U disappears. In the vacuum heat-treatment of the HA–TiO_2 system, the result also suggests that HA might react with anatase TiO_2 instead of rutile TiO_2 (Fig. 3). The reaction of HA with anatase TiO_2 occurs according to the following formula:

$$Ca_{10}(PO_4)_6(OH)_2 + TiO_2 \rightarrow 3Ca_3(PO_4)_2 + CaTiO_3 + H_2O \quad (2)$$

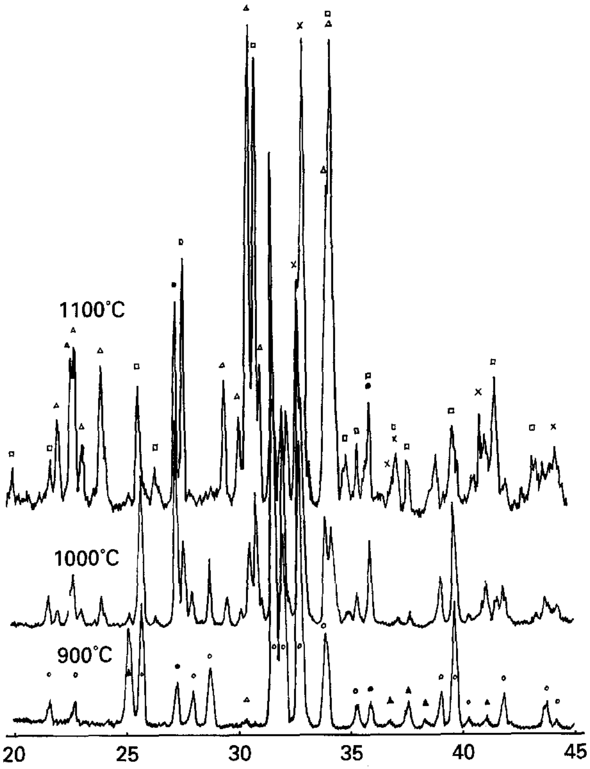

Figure 2 The XRD patterns of a HA–TiO_2 mixture sintered in air at different temperatures for 60 min, showing that TiO_2 6T remains approximately unchanged, while TiO_2 12U disappears completely. (○ HA; △ α-TCP; □ β-TCP; × $CaTiO_3$; ● TiO_2 6T; ▲ TiO_2 12U.)

The low-temperature phase β-TCP of tricalcium phosphate transforms into high-temperature phase α-TCP at about 1120 °C [9]. the α-TCP appearing below 1120 °C in the present experiments comes directly from the decomposition of HA structure instead of the transformation of β-TCP. In contrast, Lacout *et al.* [10] heated TiO_2 and HA powder together in air for 24h at 1000 °C and produced calcium titanate ($CaTiO_3$) and β-TCP with no α-TCP. The absence of α-TCP suggests its complete transformation into β-TCP because of the long heating time in air. To investigate the transformation of α- into β-TCP, vacuum heat-treatment was applied to a HA–TiO_2 system. Fig. 3 is the XRD pattern of the mixture of HA and TiO_2 heated in vacuum at 1000 °C for 30 min. Besides the same phase of $CaTiO_3$ as appears in the air case, there exists only α-TCP with no β-TCP. This difference in the resultant form of TCP suggests that the destruction of the HA structure induced by TiO_2 results in $CaTiO_3$ and the high temperature phase α-TCP as the immediate phases, and the appearance of β-TCP in the HA–TiO_2 system after in-air heat treatment results from the transformation of α-TCP induced by the water molecules in air. de Groot [11] reported that water promoted the transformation of α- into β-TCP when α-TCP was immerged in water solution.

Fig. 4 shows that the HA structure, when heated at 1300 °C for 60 min in air, started to decompose, with the appearance of traces of α-TCP. α-TCP is known as a high temperature phase with a looser structure and higher internal energy than β-TCP, but it has a lower configurational entropy than β-TCP because of a crystallographically ordered structure [12]. This lower configurational entropy makes α-TCP a more favourable phase than β-TCP at elevated temperatures. Thus, it is not surprising that α-TCP is the immediate phase rather than β-TCP when HA structure is destroyed at higher temperature.

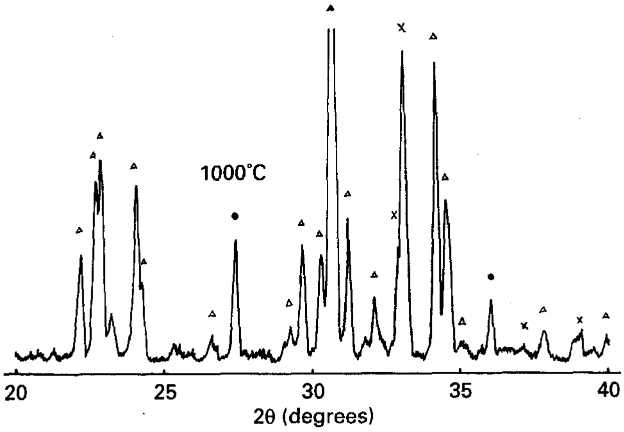

Figure 3 The XRD pattern of HA–TiO_2 mixture sintered in vacuum at 1000 °C for 30 min, showing TiO_2 12U disappears completely while TiO_2 6T still exists. (△ α-TCP; × $CaTiO_3$; ● TiO_2 6T.)

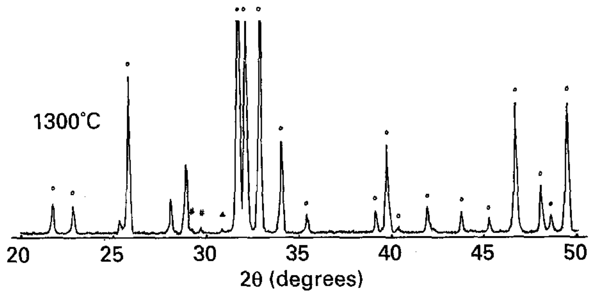

Figure 4 The XRD pattern of HA sintered in air at 1300 °C for 60 min. (○ HA; △ α-TCP; # TCPM.)

Moreover, the pressed plate of the mixtures of HA separately with ZrO_2 and Y_2O_3 were calcined in air at 1100 °C for 2 h, and their XRD patterns showed no additional peaks besides those corresponding to the reflection of phases of the starting materials themselves. Therefore, it is concluded that the thermal stability of HA is not influenced by ZrO_2 and Y_2O_3.

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