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Synthesis and characterization of functional gradient materials using Indian corals

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The partial conversion of coralline hydroxyapatite (HA) into tricalcium phosphate (TCP) catalyzed by the thermal decomposition of silver oxide was investigated. The thermal analysis of HA powder mixed with 5 mol % Ag_2O indicated the decomposition of silver oxide to be around 550 °C in the presence of HA. Subsequently a functional gradient structure was formed by spreading silver oxide on one surface of the HA compact of diameter 10 mm and then firing at 700 °C in air. The X-ray powder diffraction analysis confirmed the formation of α-TCP induced by the Ag_2O decomposition. The content of α-TCP of the sintered pellet was found to decrease with the increasing depth from the surface of the pellet. *In vitro* solubility study in phosphate buffer of pH 7.2 showed the stability of the biphasic material as in between HA and TCP.

1. Introduction

Hydroxyapatite (HA) is the major mineral component of the calcified tissues [1]. Synthetic hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] being bioactive (i.e. forms direct bond with the bone) is found to be an attractive substitute for human bone and teeth [2, 3]. Due to its weak mechanical properties it is mainly used as coatings on the surface of metallic implants such as titanium and stainless steel [4] or as composites having better mechanical properties with HA as matrix [5]. At high temperatures, for e.g. during spray coating on metallic implants, hydroxyapatite decomposes to tricalcium phosphate (TCP). Tricalcium phosphate [$Ca_3(PO_4)_2$], has been used as bone replacing material for decades although it is bioresorbable by the body fluids [2]. But the TCP is resorbed in an unpredictable way in very short time depending on its crystallinity, morphology, surface area and particle size [6]. Hence a combination of both HA and TCP, called biphasic calcium phosphate (BCP) ceramics for better bone formation and ability for bone bonding has been suggested [7]. The BCP ceramics of different HA/TCP ratio have been developed to control the resorbability of the material and at the same time to maintain its osteoconductive properties [8].

Conventionally the BCP ceramics have been prepared by mixing the pure phases of HA and TCP powders. A functionally graded form of BCP has also been formed by sintering a diamond coated HA compact at 1280 °C under reduced pressure which showed a compositional variation of HA and TCP from top to bottom of a sintered pellet [9]. The functional gradient materials (FGM) provides better circumstances for bone formation and the subsequent bone bonding mechanism. The spontaneous combustion of diamond powder leads to the partial decomposition of HA to α-TCP [9]. The FGM form of implants allows for the combination of mechanical strength of titanium and bioactivity of calcium phosphates. The thermal decomposition of HA was also found to be induced by titanium and its oxide [10] but results in the formation of impurity phases such as calcium titanate and calcium oxide. Silver and its compounds have been widely used for their pharmacological and antibacterial properties [11–13]. Silver oxide decomposes to metallic silver around 450 °C. So it is hypothesized that the decomposition of silver oxide may induce the partial conversion of HA to TCP and the silver particles also provide considerable reinforcement to HA [14].

The aim of the present study is to form a functional gradient structure of calcium phosphates induced by the decomposition of silver oxide. In continuation of our effect to develop value added product like biomaterials from the corals of Indian coast, the coralline hydroxyapatite obtained from these corals are used in this study. The porous skeleton of calcium carbonate of the corals allows the bone tissue ingrowth making direct integration with the bone possible [15]. The coralline hydroxyapatite (HA) prepared by the hydrothermal reaction of the coral retains the porous structure for the better vascular activities.

2. Materials and Methods

2.1. Material preparation

The conversion of coralline hydroxyapatite (HA) from the coral genus ''Goniopora'' species by hydrothermal

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treatment is described elsewhere [16]. In brief the corals collected from the Indian Coast were washed, dried and heated to 900 °C for 2 h to remove the organic matter and impurities. The coral powder was reacted with diammonium hydrogen orthophosphate and water under hydrothermal conditions for few hours to form hydroxyapatite. The resultant HA powder was mixed with 5 mol% of silver oxide and the thermal analysis of mixture was carried out to optimize the sintering temperature. The HA-Ag_2O powder mixture was heat treated at different temperatures between 600–800 °C in a tubular furnace at a heating rate of 20 °C/min in air. The dwell time at the maximum temperature was 12 h and the powders were furnace cooled. An FGM was fabricated by spreading the silver oxide powder on the surface of the HA green compact of 10 mm diameter and 4 mm thickness packed under a pressure of 150 MPa. The green compact was then sintered at 700 °C for 12 h in air and the pellet was removed after cooling to room temperature. The powders were collected from the top, middle and bottom regions of the sintered pellet for analysis. The schematic representation of the FGM formation is shown in Fig. 1.

2.2. Characterization

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the HA powder mixed with 5 mol% Ag_2O was performed using Perkin-Elmer PE-7 Series, USA, with a heating rate of 10 °C per min under flow of nitrogen gas. The powders from the FGM pellet were examined with a high resolution X-ray powder diffractometer (XRD) in Guinier geometry with a monochromatic CuK_α radiation using the instrument XRD 3000, Seifert, Germany. The X-ray diffraction patterns were recorded in steps of 0.01° with a counting time of 1 sec at each step. The *in vitro* solubility of the powders were carried out in phosphate buffered solution of pH 7.2. The test was carried out in an thermostated water bath at 37 °C and the change in the pH values of the phosphate buffered solution was recorded at pre-defined intervals of time.

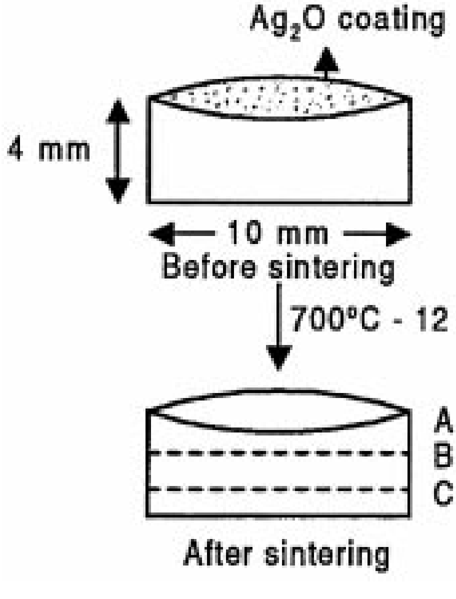

Figure 1 Schematic representation of the FGM formation showing the silver oxide spread on the HA compact and the regions of powder collection (A, B and C) after sintering at 700 °C.

3. Results and discussion

The effect of thermal decomposition of silver oxide in HA matrix has been investigated. Initially the thermal analysis of pure silver oxide was carried out to check the decomposition temperature. The DTA trace of silver oxide as shown in Fig. 2(a) exhibits two endo peaks around 460 °C and 950 °C which can be assigned as corresponding to the thermal decomposition of silver oxide to metallic silver and the subsequent melting of silver respectively. The DTA traces of both pure HA and HA-Ag_2O powder mixture are also shown in Fig. 2. The HA-Ag_2O mixture shows an endo peak at 520 °C due to the decomposition of Ag_2O in the presence of HA. The increase in the decomposition temperature of silver oxide may be due to the effect of HA matrix. The DTA trace of pure HA do not show any endo or exo peaks upto 1100 °C. Thus, heating the HA-Ag_2O mixture at temperatures well above 520 °C may result in the partial decomposition of HA induced by Ag_2O decomposition.

The thermal decomposition of silver oxide in the HA matrix was also confirmed by thermogravimetric analysis. The TGA traces of pure HA and HA-Ag_2O mixture are shown in Fig. 3. Although both the samples exhibit a major weight loss above 100 °C, the HA-Ag_2O powder mixture in addition shows a small weight loss at 500 °C as clearly indicated by the differential TGA trace. The initial weight loss around 140 °C is attributed to the evaporation of absorbed moisture in the porous HA powder. The weight loss at 500 °C may be due to the decomposition of Ag_2O in the HA matrix as also indicated by the DTA trace. As the decomposition of silver oxide was anticipated to convert HA into TCP, the sintering temperature of HA-Ag_2O compact was fixed well above 500 °C based on thermal analysis results.

The X-ray diffractograms of HA-Ag_2O powders sintered at 600, 700 and 800 °C are shown in Fig. 4. The partial decomposition of HA is observed by the presence of the α-TCP peaks and a trace of metallic silver peak is seen in the sintered powder mixtures. The

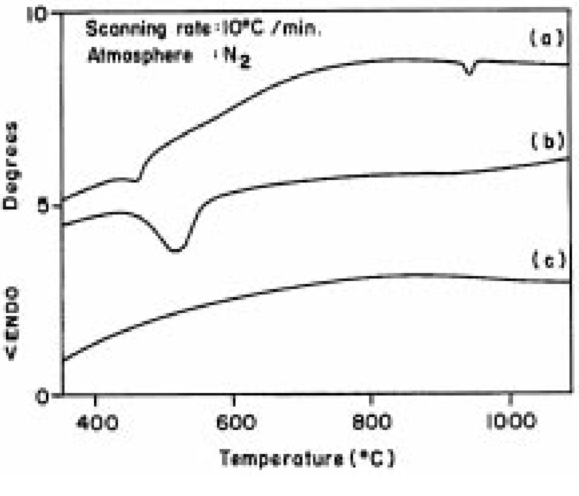

Figure 2 DTA trace of (a) pure Ag_2O, (b) HA mixed with 5 mol wt % Ag_2O and (c) pure HA powder.

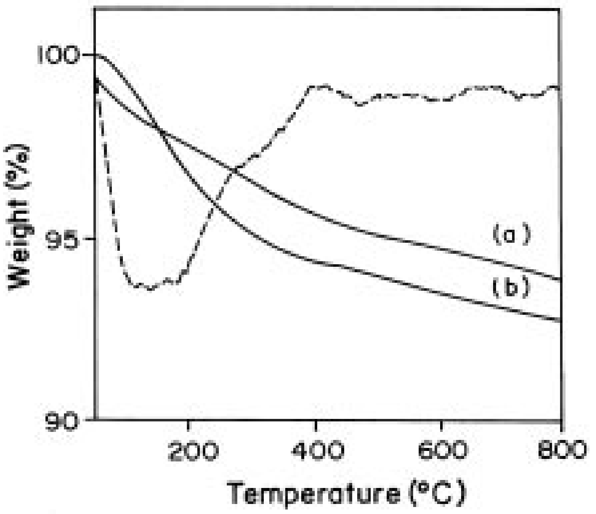

Figure 3 TGA trace of (a) Pure HA (b) HA mixed with 5 mol wt. % Ag_2O powder and (- - - -) indicates the first derivative of the curve (b).

HA-Ag_2O compact disc was prepared by spreading silver oxide powder on the surface of HA compact and sintering at 700 °C in air for a dwell time of 12 h. The pure coralline HA powder was also subjected to heat treatment under the identical conditions for reference. The powders were collected from the top, middle and bottom layers of the pellet and were subjected to X-ray powder diffraction analysis. The XRD patterns of the samples are shown in Fig. 5 along with the pure HA preheated to 900 °C. The diffraction patterns of the samples from the pellet exhibit additional peaks other than HA, which decreases with the increasing depth from the surface of the pellet. The pure HA heated to 900 °C do not show any sign of decomposition.

The thermal decomposition of apatite can generally occur in the following ways

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 2Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O \quad (1)$$

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

In both the reactions, the major decomposition product is TCP besides tetracalcium phosphate (TTCP) or calcium oxide (CaO). The formation of TTCP occurs at high temperatures and the formation of CaO results if the Ca/P ratio is slightly higher than the stoichiometric apatite [17]. But the XRD patterns do not show any trace of these phases in the present study. One of the reason may be the detection limit of the X-ray instrument. Rather, larger amounts of the decomposition products was obtained in the diamond combustion method on HA to detect CaO phase [9]. The difficulty of finding TTCP peaks is in part, due to the overlap of the main TTCP peaks [(0 4 0) and (0 1 3) peaks] with HA peaks [(2 1 1) and (3 0 0) peaks]. However, both the TTCP and CaO impurities if at all present, can be removed by washing with water as they are very soluble.

The additional peaks other than HA obtained in these patterns were identified as to be due to α-tricalcium phosphate. The amount of TCP was found to decrease from the top region (coated surface) of the compact disc to the bottom region indicating a compositional gradient from the surface to the interior of the pellet, indicating varying Ca/P ratio from top to the bottom of the pellet. The expanded pattern of the compact disc powders for the main peak regions of HA and α-TCP are shown in Fig. 6. The difficulty arises since most of the peaks of α-TCP overlaps either with β-TCP peaks or with HA peaks. The thermal decomposition of HA to α-TCP was also observed by the diamond combustion method [9]. But the diamond combustion temperature was above 1000 °C typically considered to be the decomposition temperature region of HA in vacuum. So, the formation of α-TCP at lower temperatures such as around 700 °C as seen from the figure has been induced by the thermal decomposition of silver oxide on the HA compact.

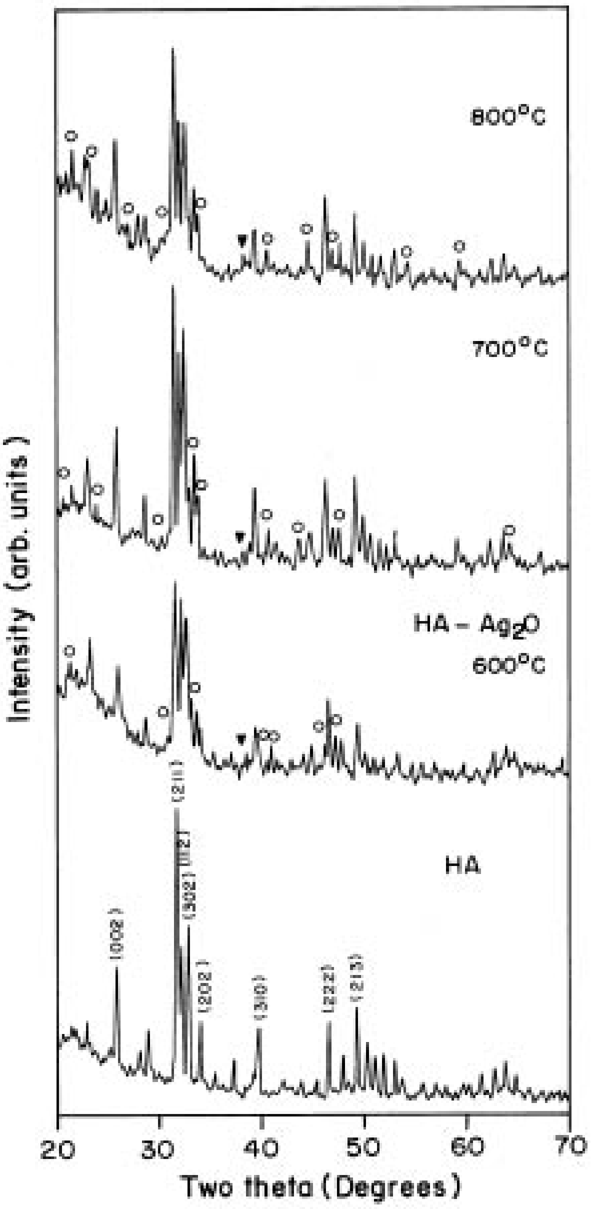

Figure 4 X-ray diffractograms of HA-Ag_2O powder sintered at various temperatures (○) α-TCP peaks (▲) Ag peak.

The decomposition product of HA leads to the formation of β-TCP in air and to α-TCP in vacuum or on quenching. The lower temperature phase β-TCP transforms to α-TCP at about 1120 °C [18]. The α-TCP known as the high temperature phase with a looser structure has a lower configurational entropy than β-TCP because of a crystallographically metastable ordered structure. This makes α-TCP a more favorable phase

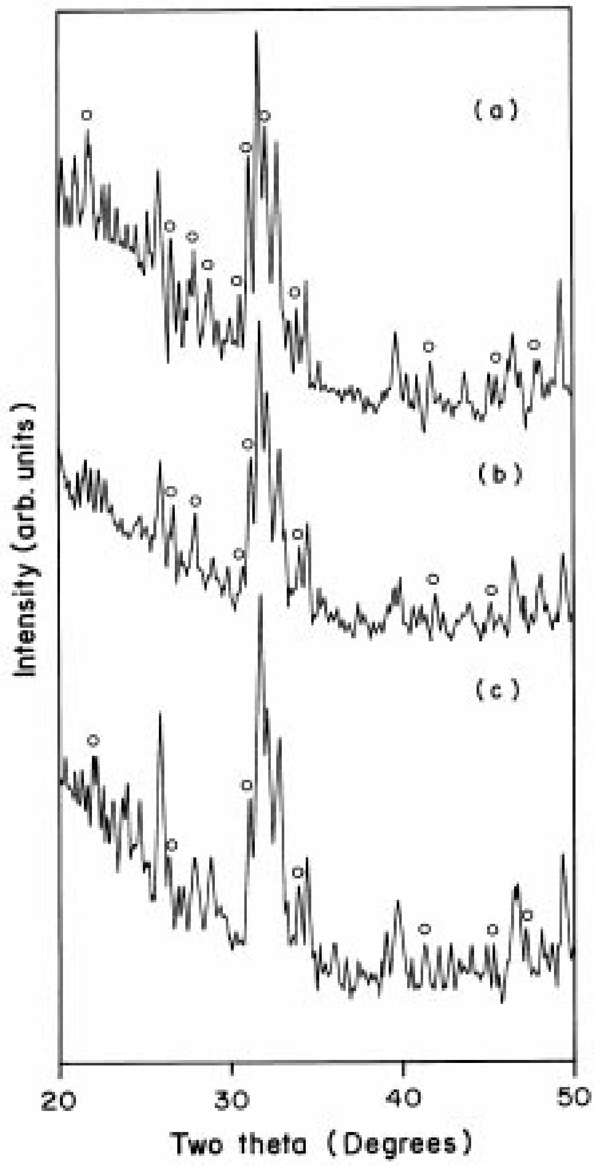

Figure 5 XRD patterns of the powders of sintered HA-Ag_2O pellet (a) top layer, (b) middle layer and (c) bottom layer. (○) α-TCP peaks.

rather than β-TCP during the thermal decomposition of hydroxyapatite at higher temperatures [10]. So, it is not surprising that the α-TCP is the phase formed when HA structure is destroyed by silver oxide decomposition.

The diffraction lines corresponding to HA were indexed carefully and refined by the least square method (CELN program) and the cell parameters in all samples were obtained. The lattice parameters were found to agree with reported values of HA (JCPDS 9-432) indicating that there has been no substitution or inclusion of Ag particles in the apatite structure.

The *in vitro* stability of HA-Ag_2O powder sintered at 700 °C was carried out in phosphate buffer solution at physiological pH of 7.2 along with pure HA and TCP for comparison. The variations in the pH of the buffered solutions at 37 °C were measured at defined intervals of time till there is no further change in the pH value and are shown in Fig. 7. The HA was found to be stable in the phosphate buffer solution for a period of one week indicating its stability at physiological conditions while the TCP showed continous dissolution leading to decrease in the pH value [19, 20]. The pH of the HA-Ag_2O sintered powder varies slowly with the values between HA and TCP showing that it consists both the behavior of HA and TCP.

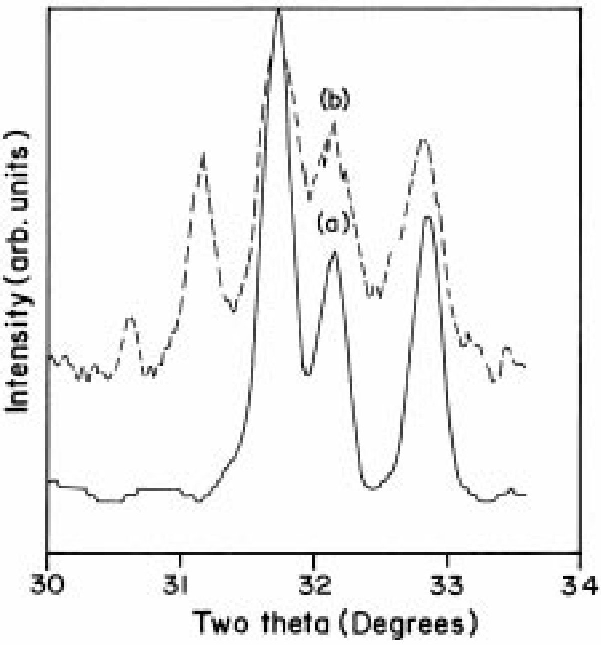

Figure 6 Expanded diffraction patterns of (a) HA and (b) top layer of the pellet.

4. Conclusion

The thermal decomposition of Ag_2O present in HA-Ag_2O mixture has influenced the partial decomposition of HA at lower temperatures. The HA-Ag_2O pellet sintered at 700 °C showed a compositional gradient of calcium phosphates of varying Ca/P ratio. The amount of TCP formed decreases from top to the bottom layer of the pellet.

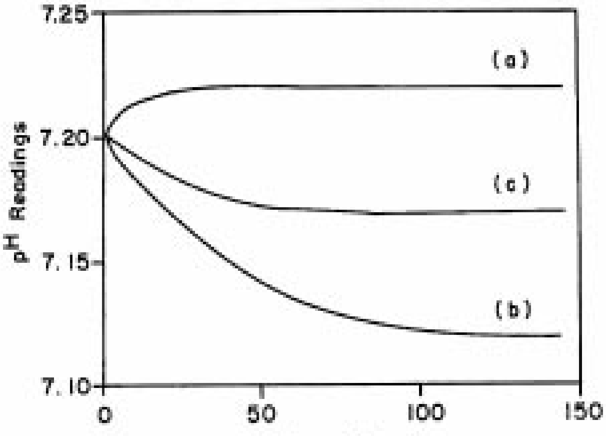

Figure 7 *In vitro* solubility studies in phosphate buffer of pH 7.2 for (a) pure HA (b) pure TCP and (c) powder from the HA-Ag_2O sintered pellet.

Acknowledgments

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