

Microstructural Improvement of Hydroxyapatite-ZrO₂ Composite Ceramics via Thermal Precipitation Techniques.

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Abstract. Hydroxyapatite-ZrO₂ composite ceramic were synthesized using a thermal precipitation techniques. The chemical precursors were prepared from di-ammonium hydrogen orthophosphate, calcium oxide (CaO) derived from chicken eggshell, zirconium dioxide (ZrO₂) and distilled water. The mixture were heated at the various temperatures from 100 to 700 °C in the furnace with an incremental temperature of 100 °C. The ZrO₂ contents in the composite ceramic were varied from 0 to 15 percent weight of CaO. The prepared composites were then annealed at 300, 600 and 700 °C for 4 h in air. The crystal structure, function group and morphology of all samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and universal testing machine (UTM), respectively. The results indicated that the undoped-ZrO₂ samples hydroxyapatite phase with a hexagonal structure. However, the hydroxyapatite was transformed to the tri-calcium phosphate after thermal treatment at 700 °C. For the doped-ZrO₂ samples, the hydroxyapatite and ZrO₂ phases were found. Moreover, the result showed that the compressive strength of hydroxyapatite-ZrO₂ composite ceramic increased with increasing the ZrO₂ content.

1. Introduction

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) is the inorganic mineral that most found in human bone and teeth and has been used as an orthopedic and dental material [1]. Although hydroxyapatite has been widely use in medical application, because it has excellent biocompatibility and bioactive properties. But, it is limited in use for some application due to lacking in the high strength [2]. Recently, researchers study and develop the methods to improvement the physical properties of hydroxyapatite. The way for improvement physical properties is incorporation the second phase [3]. Moreover, the adding second phase must dose not destruct the biocompatibility and bioactive properties of hydroxyapatite. There are several material for improvement physical properties such alumina (Al₂O₃) and zirconia (ZrO₂) [4]. Especially, ZrO₂ has variety advantages including excellent mechanical strength, wearability, resistance to corrosion and biocompatibility. It has been significantly applied in medical such as the preparation of denture, artificial bone and biological ceramic and the reparation of bone materials [5]. In this paper, the improvement of mechanical properties was investigated to prepare hydroxyapatite-ZrO₂ composite ceramics via thermal precipitation techniques, CaO derived from chicken eggshell and (NH₄)₂HPO₄ used as initial raw materials and improvement of hydroxyapatite with ZrO₂.

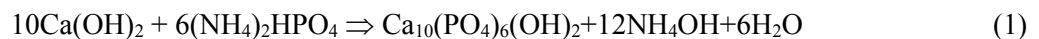
2. Methodology

The chicken eggshells obtained from canteen at King Mongkut's University of Technology Thonburi (KMUTT), Bangkok, Thailand were used as a calcium source. The di-ammonium hydrogen orthophosphate ((NH₄)₂HPO₄) purchased from Ajax Finechem company, Australia were used as a phosphate source. The chicken eggshells without inner protein membranes were washed with distill water and dried at room temperature until dry. Then, they were grounded into powder with agate mortar. Finally, the eggshells were heated at 1300°C with rate 5°C/min and transformed to calcium oxide (CaO). ZrO₂ purchased from Tosoh corporation and CaO were dissolved in the distill water. The ZrO₂ contents in the mixture were varied from 0 to 15 percent weight of CaO. In addition, CaO were transformed to calcium hydroxide (Ca(OH)₂) solution when it was dissolved in the distill water. The Ca(OH)₂/ZrO₂ solution were poured in the (NH₄)₂HPO₄ solution. The mixture was mixed and stirred by magnetic stirring for 30 min. Moreover, the mixture were heated at the various temperatures from 100 to 700 °C in the furnace for 4 h with an incremental temperature of 100 °C. The hydroxyapatite-ZrO₂ composites ceramic were formed by the Ca(OH)₂/ZrO₂ and (NH₄)₂HPO₄ solution. Furthermore, the prepared composites were then annealed at 300, 600 and 700 °C for 4 h in air. The crystal structure phases of all samples were investigated by X-ray diffraction (XRD) using Phillips PW108 with CuK α radiation generated at 30 kV and 30 mA. The function groups of all samples were measured by Fourier transforms infrared spectroscopy (FTIR, Perkin Elmer (spectra two)). The morphology of all samples characterized by field emission scanning electron microscopy (FESEM, FEI (Nova NanoSEM 450)). And, the mechanical properties of samples were evaluated by universal testing machine (UTM, Lloyd). For mechanical testing, the powder samples were weighted at 0.9 g and compressed in the 12 mm diameter of stainless mold at 3000 psi for pellet forming.

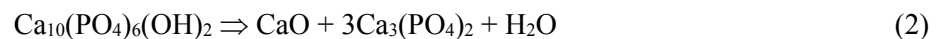
3. Results and discussion

3.1. Pure hydroxyapatite preparation via thermal precipitation technique.

The figure 1 shows the XRD pattern of sample powder various synthesizes temperature. At the 100 °C, the pure hydroxyapatite phase was found according with JCPDS file no. 09-0432. For this reason, the hydroxyapatite phase was formed by the chemical reaction between Ca(OH)₂ and (NH₄)₂HPO₄ as an equation (1) [6].



After increasing the synthesized temperature increased, the pure hydroxyapatite phase was found in XRD pattern of sample synthesized at 200 to 600 °C as same 100 °C. This result indicates that at 100 °C of synthesized temperature is enough to grow hydroxyapatite structure. However, the hydroxyapatite phase vanished after synthesized at 700 °C. But, the tri-calcium phosphate (Ca₃(PO₄)₂) according with JCPDS file no.70-2065 appear due to the hydroxyapatite transforms to it as an equation (2) [7].



The figure 2 shows the FTIR spectra of the samples powder various synthesizes temperature. The spectra show vibration bands corresponding to phosphate (PO₄³⁻) and hydroxyl (OH⁻) as summarized in Table 1. The band at 1095, 1040, 964, 601 and 562 cm⁻¹ are attributed to the PO₄³⁻. And, the band at 631 cm⁻¹ is attributed to the OH⁻ [8]. Besides, the band at 631 cm⁻¹ was not detect in the sample at 700 °C of synthesized temperature. This FTIR spectra result indicated that OH⁻ group from hydroxyapatite was decompose after synthesizing at 700 °C. Meanwhile, hydroxyapatite transform to Ca₃(PO₄)₂ similarly to the XRD results.

The figure 3 show the FESEM micrograph of the samples powder synthesized at 100, 600 and 700 °C. The hydroxyapatite particle at 100 and 600 °C are agglomerated in sphere shape with 50 nm of diameter. However, the sample synthesized at 700 °C which is the Ca₃(PO₄)₂ phase was merged from high

temperature during synthesizing. The average particle size are about at 100 nm as shown in Figure 3. The FESEM results correspond to the XRD and FTIR result.

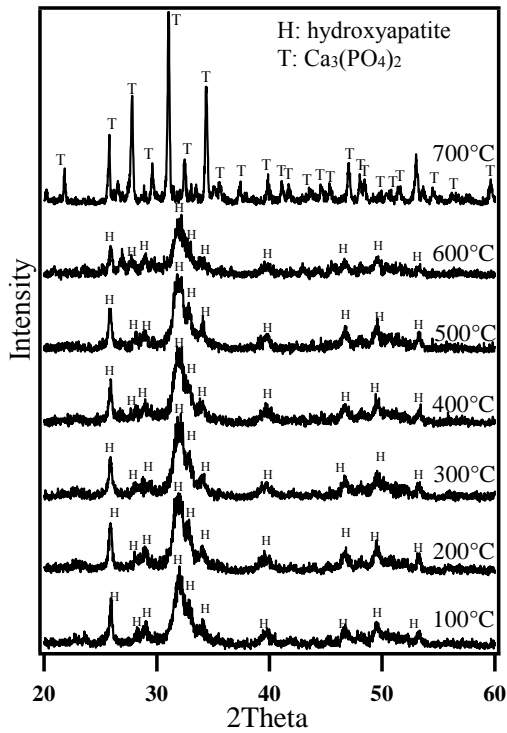


Figure 1. XRD patterns of hydroxyapatite were synthesized various temperature.

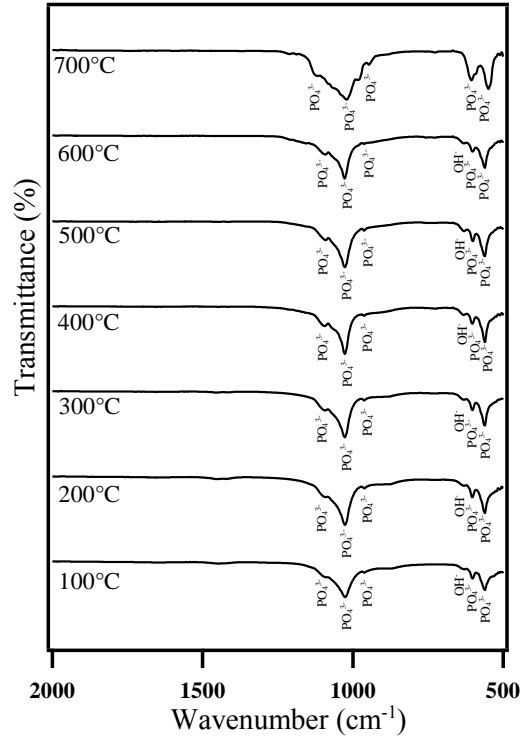


Figure 2. FTIR spectra of hydroxyapatite were synthesized various temperature.

Table 1. Observed vibrational frequencies of hydroxyapatite.

Wave number (cm ⁻¹)	Function Group
562, 601, 964	(PO ₄ ³⁻)
1040, 1095	(PO ₄ ³⁻)
631	(OH ⁻)

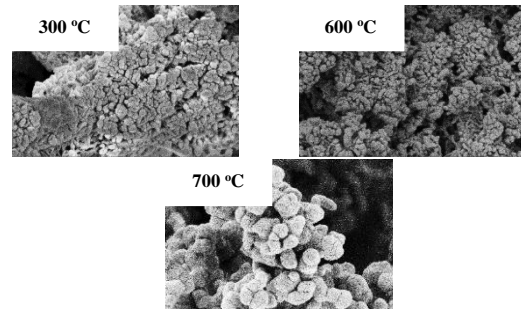


Figure 3. FESEM images of sample powder were synthesized various temperature

3.2. Hydroxyapatite-ZrO₂ composites ceramic preparation via thermal precipitation technique.

The figure 4 shows the XRD pattern of hydroxyapatite-ZrO₂ composites powder various ZrO₂ content after synthesized at 100 °C. The 0%weight of ZrO₂ content was identified only hydroxyapatite phase according with JCPDS no. 09-0432. There are no other phases was detected, such as a calcium oxide and ZrO₂ in the XRD pattern. After ZrO₂ was added, the ZrO₂ phase according with JCPDS no. 50-1089. The peak at 2theta 30.43 which is ZrO₂ major peak was increased with increasing of ZrO₂ content. On the other hand, the peaks of hydroxyapatite still appear in XRD pattern of sample various ZrO₂ content. This result indicated that adding ZrO₂ in the hydroxyapatite preparing process via thermal precipitation technique has no effect on hydroxyapatite structure.

The figure 5 shows the FTIR spectra of hydroxyapatite-ZrO₂ composites powder various ZrO₂ content after synthesized at 100 °C. The spectra show vibration bands corresponding to phosphate (PO₄³⁻) and hydroxyl (OH) as summarized in Table 1. The band at 1095, 1040, 964, 601 and 562 cm⁻¹ are attributed to the PO₄³⁻. And, the band at 631 cm⁻¹ is attributed to the OH⁻. Moreover, the sample which are added ZrO₂ content was found the vibration band at 486 cm⁻¹. Because, the hydroxyapatite-ZrO₂ composites samples consists of hydroxyapatite and ZrO₂ phases according the XRD results. So, the ZrO₂ vibration band at 486 cm⁻¹ [9] was detected in FTIR spectra.

3.3. Temperature effect on Hydroxyapatite-ZrO₂ composites ceramic.

The figure 6 shows the XRD pattern of the 15%weight of ZrO₂ content in composites powder synthesized at 100 °C. The sample were heated at 300, 600 and 700 °C for treatment. The results show that the intensity of ZrO₂ increased with increasing the heated temperature. In contrast, the intensity of hydroxyapatite decreased with increasing the heated temperature. In fact, the crystallinity of hydroxyapatite was generally increased with increasing the heated temperature. But, the crystallinity of ZrO₂ was rapidly increased than hydroxyapatite. Hence, the intensity of hydroxyapatite of composites sample was decreased when the samples were heated. Furthermore, the hydroxyapatite phase in composites sample was transform to Ca₃(PO₄)₂ phase after heat at 700 °C as a result of the hydroxyapatite deformation.

3.4. Mechanical properties of Hydroxyapatite-ZrO₂ composite ceramics.

The figure 7 shows the relative of compressive strength compare with ZrO₂ content in composites pellet. The results show that the compressive strength was increased about 1.68 times with increasing the ZrO₂ content 1%wt. Since, ZrO₂ structure has higher compressive strength than hydroxyapatite structure. So, adding ZrO₂ content produces the good mechanical properties on hydroxyapatite powder.

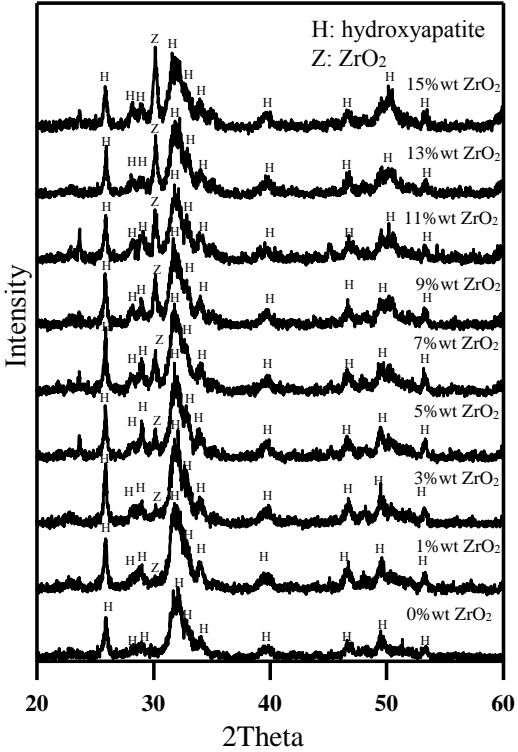


Figure 4. XRD patterns of sample powders various percent weight of ZrO₂

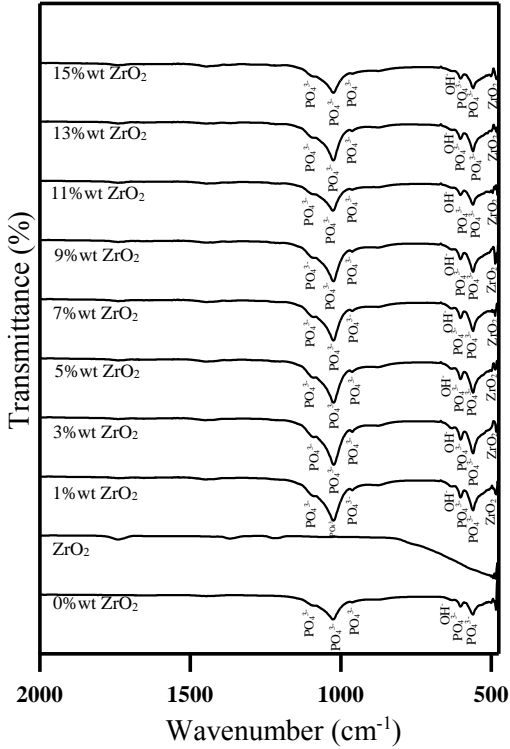


Figure 5. FTIR spectra of sample powders various percent weight of ZrO₂

