Preparation and characterization of hydroxyapatite powder and study of hydroxyapatite - alumina Composite

Ghazi K. Saeed¹, Abbas F. Essa² and Saja Abdul-Ammer Said²

¹ Science Department – College of Basic Education /University of Waist
² Physics Department – College of Science / University of Waist

Email: phyghazi@ymail.com

Abstract. Hydroxyapatite powder \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \) was prepared locally from Iraqi beef bones, and characterization the powder as well as studied purity. A composite of hydroxyapatite-alumina was also prepared with a ratio of alumina 0,5,10,15,20,25% wt. Use polyethylene glycol as a binder with 1% wt by dissolving polyethylene glycol with ethanol (1g: 100ml) at 40 °C and using a magnetic stirrer to obtain a homogeneous solution for the material. Then drying the powder and pressing to prepare compound samples, after that heat treatment at 1350°C for three hours. The physical and mechanical properties studied such as density, porosity, water absorption ratio, hardness and compression resistance, as well as X-ray diffraction and X-ray florescence. X-ray diffraction analysis showed that the hydroxyapatite phase was stabilized for all prepared samples before and after heat treatment with chemical form \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \), the hydroxyapatite showed a stabilization in phase before and after heat treatment without decomposition into different components.

Keywords: Hydroxyapatite, Alumina, Composite and Medical applications

1. Introduction

The importance of hydroxyapatite (HA) used in the many applications, especially in medical applications. Hydroxyapatite is a natural mineral form of calcium apatite, the chemical formula \( \text{Ca}_5(\text{PO}_4)_3(\text{OH}) \), but it is usually written \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \) to indicate that the crystal unit cell of two entities. Molecular weight has 502.31g/mol and hexagonal crystalline structure with dimensions \( a = 9.41 \) Å, \( c = 6.88 \) Å as shown in Figure (1). It can take several colors including white, milky, colorless, gray, yellow and yellowish green. The main components of human bones are organics, mostly collagen fibers and inorganic materials known as hydroxyapatite, which accounts for 65-70% by weight of natural bone as shown in Figure (2). Collagen fibers are responsible for bone flexibility, while the metal component (hydroxyapatite) is responsible for bone stiffness, and the molecular ratio of calcium to phosphorus ratio (\( \text{Ca}/\text{P} \)) within hydroxyapatite in bone tissue is around 1.67 [1-3].

Calcium Phosphate (CaP) is widely used directly in solid tissues (eg bone) and in various medical applications, which can be used as compensation for solid tissues. There are many types of calcium phosphate such as hydroxyapatite (HA), tetra- calcium phosphate (TTCP), tri-calcium phosphate (TCP), anhydrous dia-calcium phosphate (DCP), amorphous- calcium phosphate (ACP), binary-calcium phosphate (BCP). Hydroxyapatite (HA) is the most promising and good material for bone replacement for its consistency and biocompatibility [4]. Several methods were used to prepare hydroxyapatite, including precipitation, sol-gel, hydrothermal technique, biomimetic deposition, electro deposition, Animal bones directly, and other methods [5]. When the samples are formed in any way and the thermal treatment is performed, and after the temperature exceeds 1100°C, hydroxyapatite...
breaks up into several compounds such as $\beta$-$\text{Ca}_3(\text{PO}_4)_2$, called $\beta$-TCP $[6-9]$. It can dissolve according to the following reactions $[10, 11]$.

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow \text{Ca}_4\text{P}_2\text{O}_{19} + 2\text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O} \quad \cdots (1)
\]

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \leftrightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaO} + \text{H}_2\text{O} \quad \cdots (2)
\]

Hydroxyapatite can be used as a coating for all parts of the human body. Complete parts of the human body can also be prepared as parts of the bone, teeth, face, jaws and skull. It also enters the cosmetic processes of many parts of the body. In addition can enter a large proportion in the preparation of animal feed $[12]$.

Figure (1) crystalline structure of hydroxyapatite $[2]$  
Figure (2) The proportions of organic and inorganic substances $[3]$

2. Experimental Work

2.1. For the purpose of preparing the hydroxyapatite powder locally, follow the following steps:

Iraqi beef bones were prepared from local markets and first cleaned from the meat and fat residues, boiling the bones with water for five hours and more than once to remove the fat, drying the bones with the electric dryer at 75 °C for 24 hours, cracking bones into small pieces using an iron hammer, putting the broken bones in a ceramic package and conduct the process of heat treatment through calcinations at 750°C for four hours, and make sure that all broken bones lost organic materials and became a pure white milky black color, after thermal treatment, the bone was milled using a rotary mill with iron blades, sifting the powder with a particle size of less than 150 μm using sieves. Conducting analysis for the diagnosis of the substance and phase using the XRD diffraction system. Materials and impurities introduced in the structure of hydroxyapatite verified through the XRD for American hydroxyapatite powder was used for comparison purposes, in addition to the standard spectra, which is included with the system within the x-ray diffraction library.

2.2. Preparation of samples:

To Preparation of a composite of hydroxyapatite-alumina with alumina ratios 0,5,10,15,20,25% wt, the alumina used from ALM-41-SUMITO-CHEMICAL-COMPANY-UK, which screening the powder with a particle size of less than 150 m using sieves, using following steps.
Polyethelenglycol (SIGMA-ALDRICH-WG) with a molecular weight of 6000 was used as a bond material by dissolving polyethelenglycol with alcohol ethanol (1g: 100ml) and at 40°C. Using a magnetic stirrer, the magnet movement moves the solution continuous to obtain a homogeneous solution. The ratio of the polyethylene solution was used for the preparation of mixtures of hydroxyapatite - 99% wt against the bonding material by 1% wt and by using the magnetic mixer for the purpose of obtaining a homogeneous solution. Drying the solution containing the materials using a dryer at 75°C heat for 24 hours. Compressing the samples using a 9mm metal mold and a pressure of 2.75Ton to compress the samples in a semi-dry form. Special program for thermal treatment to samples as shown in Figure (3).

![Figure (3) Thermal treatment program](image)

2.3. Analysis:

X-ray diffraction tests for the purpose of determining the type and phase of the material. Figure (4) shows that the material is hydroxyapatite with phase is hexagonal by comparing to the USA-spectra and the standard spectra with the card number (34-0010). There is almost perfect match between the three spectra. In addition, X-ray diffraction tests were conducted for one of the samples prepared at the thermal treatment at 1350°C for three hours. The tests showed that the material is hydroxyapatite without any disintegration into other components as shown in Figure (5). XRF tests show that the main materials in the analysis are phosphorus oxides (P₂O₅) and calcium oxides (CaO). This confirms that the predominant material is hydroxyapatite and other substances with low ratios, and this is expected in bone components as in Table (1). The molecular ratio of calcium to phosphorus ratio (Ca/P) was found 1.71 which approximately compatible to references [1-3]. Green density measured with pressure to choose the best pressure for forming the samples as shown in Figure (6). Density tests with the temperature of the different thermal treatment at a time of three hours as in Figure (7). The following tests were performed: radial shrinkage (diameter contraction), hardness of Vickers, compressive strength, apparent density, porosity and water absorption ratio as shown in Figures (8-13).
Figure (4) X-ray diffraction spectra of HA-powder USA- powder, prepared and standard
Figure (5) Represent the X-ray diffraction spectra of the hydroxyapatite sample alone at heat treatment 1350°C for three hours.

Figure (6) Change green density with pressure

Figure (7) Bulk density with the temperature
Figure (8) Change radial shrinkage with alumina

Figure (9) Vickers hardness with alumina

Figure (10) Change compressive strength with alumina

Figure (11) Apparent density with alumina

Figure (12) Change porosity with alumina

Figure (13) Change water absorption with alumina
Table (1) shows the results of the x-ray fluorescence of the hydroxyapatite

| Z  | Symbol | Element       | Norm. Int. | Concentration | Abs. Error |
|----|--------|---------------|------------|---------------|------------|
| 12 | MgO    | Magnesium     | 113.8378   | 3.131 %       | 0.046 %    |
| 13 | Al2O3  | Aluminum      | 0.0000     | < 0.0038 %    | (0.0) %    |
| 14 | SiO2   | Silicon       | 0.0000     | < 0.0011 %    | (0.0) %    |
| 15 | P2O5   | Phosphorus    | 31550.8606 | 31.37 %       | 0.02 %     |
| 16 | SIO3   | Sulfur        | 624.2428   | 0.3879 %      | 0.0013 %   |
| 17 | CI     | Chlorine      | 708.2183   | 0.7756 %      | 0.0023 %   |
| 18 | K2O    | Potassium     | 0.0000     | < 0.0012 %    | (0.0) %    |
| 20 | CaO    | Calcium       | 12892.4394 | 53.90 %       | 0.04 %     |
| 22 | TiO2   | Titanium      | 1.4561     | 0.0086 %      | 0.0021 %   |
| 23 | V2O5   | Vanadium      | 0.4519     | < 0.0061 %    | (0.0060) % |
| 24 | Cr2O3  | Chromium      | 4.1424     | < 0.0015 %    | (0.0) %    |
| 25 | MnO    | Manganese     | 0.6879     | 0.0098 %      | 0.0030 %   |
| 26 | Fe2O3  | Iron          | 97.8309    | 0.03731 %     | 0.00632 %  |
| 27 | CoO    | Cobalt        | 0.0803     | < 0.00039 %   | (0.0) %    |
| 28 | NO2    | Nickel        | 13.9385    | 0.00331 %     | 0.00012 %  |
| 29 | CuO    | Copper        | 21.9924    | 0.0441 %      | 0.00013 %  |
| 30 | ZnO    | Zinc          | 181.5375   | 0.2709 %      | 0.0018 %   |
| 31 | Ga     | Gallium       | 5.5332     | 0.0052 %      | 0.00008 %  |
| 32 | Ge     | Germanium     | 0.0000     | < 0.00005 %   | (0.0) %    |
| 33 | As2O3  | Arsenic       | 0.0000     | < 0.00007 %   | (0.0) %    |
| 34 | Se     | Selenium      | 0.0000     | < 0.00005 %   | (0.0) %    |
| 35 | Br     | Bromine       | 9.5250     | 0.00343 %     | 0.00002 %  |
| 37 | Rb2O   | Rubidium      | 4.0470     | 0.00312 %     | 0.00002 %  |
| 39 | SrO    | Strontium     | 2621.3961  | 0.07414 %     | 0.00012 %  |
| 99 | Y      | Yttrium       | 916.2335   | 0.02117 %     | 0.00006 %  |
| 40 | ZrO2   | Zirconium     | 908.6147   | 0.4376 %      | 0.0011 %   |
| 41 | Nb2O5  | Niobium       | 0.0000     | < 0.00014 %   | (0.0) %    |
| 42 | Mo     | Molybdenum    | 0.0000     | < 0.00010 %   | (0.0) %    |
| 47 | Ag     | Silver        | 0.0000     | < 0.00022 %   | (0.0) %    |
| 48 | Cd     | Cadmium       | 0.7717     | < 0.00020 %   | (0.0) %    |
| 50 | SnO2   | Tin           | 9.7564     | 0.00224 %     | 0.00014 %  |
| 51 | Sb2O5  | Antimony      | 8.8373     | 0.00329 %     | 0.00018 %  |
| 52 | Te     | Tellurium     | 10.6962    | 0.00229 %     | 0.00012 %  |
| 53 | I      | Iodine        | 0.0000     | < 0.000030 %  | (0.0) %    |
| 55 | Cs     | Cesium        | 0.0000     | < 0.00040 %   | (0.0) %    |
| 56 | Ba     | Barium        | 12.1451    | 0.00042 %     | 0.00078 %  |
| 57 | La     | Lanthanum     | 0.0000     | < 0.00020 %   | (0.0) %    |
| 58 | Ce     | Cerium        | 0.0000     | < 0.00020 %   | (0.0) %    |
| 68 | Er     | Erbium        | 0.0000     | < 0.00061 %   | (0.0) %    |
| 70 | Yb     | Ytterbium     | 0.0552     | < 0.00020 %   | (0.0) %    |
| 72 | Hf     | Hafnium       | 19.4467    | 0.00049 %     | 0.00018 %  |
| 73 | Ta2O6  | Tantalum      | 22.0777    | 0.00868 %     | 0.00026 %  |
| 74 | WC3    | Tungsten      | 1.4712     | < 0.00018 %   | (0.0) %    |
| 80 | Hg     | Mercury       | 0.4720     | < 0.00010 %   | (0.0) %    |
| 81 | Ti     | Titanium      | 2.0335     | 0.00014 %     | 0.00003 %  |
| 82 | PbO    | Lead          | 7.0797     | 0.00075 %     | 0.00005 %  |
| 83 | Bi     | Bismuth       | 0.0000     | < 0.00010 %   | (0.0) %    |
| 90 | Th     | Thorium       | 5.7943     | 0.00041 %     | 0.00004 %  |
| 92 | U      | Uranium       | 4.9709     | < 0.00010 %   | (0.0) %    |

Sum of concentration 89.52 %
3. Discussion

The X-ray diffraction in Figure (4) shows that the prepared samples is hydroxyapatite and the phase is hexagonal phase by comparing with USA spectrum and the standard spectra of card number (34-0010). And its color is milky white and its purity is high through the results of the XRF tests shown in Table (1). When the percentage of loss (loi) of 10.48% wt was left, the ratio of calcium oxide was 59.92% wt and the ratio of phosphorus oxide was 35.04% wt and the total ratio became 94.96% wt. The remaining percentage is for other substances. These results indicate that the main components of hydroxyapatite are calcium oxide and phosphorus oxide and this is consistent with the hydroxyapatite compound Ca_{10} (PO_{4})_{6} (OH)_{2}. Figure 5 shows that the X-ray diffraction spectra of the sample prepared at 1350 °C for three hours preserves the hydroxyapatite phase by comparing with the standard spectra, this is due to the thermal treatment program chosen, and this is very useful in the various applications of hydroxyapatite. Most of the literature refers to the breakdown of hydroxyapatite when conducting heat transactions that exceed 1100ºC [6-8]. Figure (6) represents the change of green density with the different values of pressing; the pressure of 2.75ton was selected for preparing the samples. Figure (7) represents the change in density with temperature; the results showed that the best temperature was 1350°C for three hours. Figure (8) represents the change in the radial shrinking with the alumina ratios and shows a linear decrease with the ratios due to the fact that by increasing the alumina ratio, we need a temperature higher than 1350°C for which the material granules are combined to complete the sintering process. Figure (9) represents the change in Vickers hardness with alumina ratios, the highest hardness value is shown in 5% wt of alumina ratio, there was a decrease in the hardness values for the same reason, which is not enough for the sintering temperature, and the hardness values are consistent with reference values [8]. Figure (10) represents the compression strength with alumina ratios and through the form shows a decrease in values with increased alumina ratios due to low temperature of sintering and results consistent with reference values [6]. Figure (11) represents the change in the apparent density with the alumina ratios; the results show a decrease in the density ratios as the other properties, the reason is the same as mentioned above despite the increase in the alumina ratios, whose theoretical density of alumina is higher than the density of hydroxyapatite. The Figures (12) and (13) represent the change in porosity and water absorption rate and their behavior as expected to reverse the behavior of the apparent density. The shapes show that the less porosity and absorption of water is at the hydroxyapatite alone to achieve the appropriate degree of sintering.

4. Conclusion

The powder is characterized as hexagonal hydroxyapatite, milky white, high purity, can be easily grinded and sieving (screened) to obtain the desired particle size, stable with time and weather conditions. The best properties were pure hydroxyapatite, except for the Vickers hardness, which had the highest value at 5% wt of alumina. Also, phase-hydroxyapatite was preserved before and after thermal treatment by selecting the heat treatment program.

5. References

[1] Sobczak-Kupiec A, Malina D, Kijkowska R and Wzorek Z. 2012 Comparative Study of Hydroxyapatite Prepared by the Authors With Selected Commercially Available Ceramics, Digest Journal of Nanomaterials and Biostructures, Vol. 7, No 1, January - March, pp. 385 – 391.
[2] Uddin M H, Matsumoto T, Okazaki M, Nakahira A and Sohmura T 2010 Biomimetic fabrication of apatite related biomaterials, book edited by Amitava Mukhergee, ISBN 978-953-307-025-4, Published: under CC BY-NC-SA-3.0 license.

[3] Azmat O and Nagtode P P 2015 Hydroxyapatite Crystal Deposition Disease-An Indepth Analysis to Improve Understanding and Facilitate Symptomatic Relief, DOI: 10.1594/essr2015/P-0106.

[4] Pal S, Roy S and Bag S 2005 Hydroxyapatite Coating over Alumina -Ultra High Molecular Weight Polyethylene Composite Biomaterials, Trends Biomater. Artif. Organs, Vol 18 (2), January, pp. 106-109.

[5] Nayak A K 2010 Hydroxyapatite Synthesis Methodologies: An Overview . International Journal of ChemTech Research, Vol.2, No.2, April-June, pp 903-907.

[6] Hannora A E 2014 Preparation and Characterization of Hydroxyapatite/ Alumina anocomposites by High-Energy Vibratory Ball Milling. J. Ceram. Sci. Tech., 05 [04], pp 293-298.

[7] Shekhar N, Krishanu B, Kaishi W, Rajendra K B and Bikramjit B 2010 Sintering, Phase Stability, and Properties of Calcium Phosphate-Mullite Composites, J. Am. Ceram. Soc., 93 [6], pp1639–1649.

[8] Bulut B , Demirkol N, Erkmen Z E and Kayali E S 2015 Comparison of Microstructural and Mechanical Properties of Hydroxyapatite-Al2O3 Composites with Commercial Inert Glass (CIG) Addition, ACTA PHYSICA POLONICA A Vol. 127, No. 4, pp1094-1096.

[9] Pujiyanto E , Tontowi1 A E, Wildan M W and Siswomihardjo W 2012 Porous Hydroxyapatite–Zirconia Composites Prepared by Powder Deposition and Pressureless Sintering, Advanced Materials Research Vol. 445 pp 463-468.

[10] Aminzare M, Eskandarib A, Baroonian M H, Berenov A, RazaviHesabi Z, Taheria M and Sadrnezhaad S K 2013 Review paper: Hydroxyapatite nanocomposites: Synthesis, sintering and mechanical properties, Ceramics International 39 pp 2197–2206.

[11] Mohsen E , Touradj E and Esmail S 2012 Effect of Sintering Atmosphere on Phase Evolution of Hydroxyapatite Nanocomposite Powders, PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES, Vol. 1 No 2, 02NNBM05(3pp).

[12] Mohamaddoost F, Yusoff H M, Matori K A, Ostovan F and Vahedi G R 2014 Bio Ceramic Zirconia/Hydroxyapatite Nano Composite Extracted from Bovine Bone, Australian Journal of Basic and Applied Sciences, 8(15) Special, pp 302-306.

[13] Pertti A 1996 Mechanical and Physical Properties of Engineering Alumina Ceramic, VTT TIEDOTTEITA – MEDDELANDEN – RESEARCH NOTES 1792 , TECHNICAL RESEARCH CENTER OF FINLAND ESPOO, PP 1-26.