Investigation of Hydrothermal Processing of Strontium Peroxyapatite Synthesis

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Keywords: strontium peroxyapatite, hydrogen peroxide, permanganatometric titration, hydrothermal processing

Abstract

The experimental research was devoted to the peroxide ions' incorporation in strontium hydroxyapatite (SrHAp) by exposure to 50 % wt. H_2O_2 during hydrothermal processing in the closed steel vessel system under relatively mild conditions at temperature range from 150 to 110 ^oC. Peroxide enriched strontium apatite (SrPerAp) was subjected to quantitative chemical analysis - content of peroxide was determined by classical permanganometric titration and stability of peroxide content was evaluated within three months. The structure of synthesised powders was characterized with X – Ray Difraction. This study continued from the previous ones. The objective was to obtain apatite, with a higher peroxide ion content incorporated in apatitic channels of strontium substitute lattice with synthesis at notably lower temperature and shorter time.

Introduction

Hydroxyapatite, (HAp), $[Ca_{10}(PO_4)_6(OH)_2]$ is one of the most promising biomaterials among all the calcium orthophosphates. Since chemically synthesized apatite indicates structure similarities to naturally formed mineral fraction of bone, HAp become one of the main bioceramics. In addition HAp exhibits several practical applications as a catalyst, LC column, lighting material or chemical sensor. But more essential is its emploing in clinical applications for bone and dental regeneration due to its excellent biocompability [1].

Cationic and anionic substitutions of initial calcium phospate can enrich the hosting material with additional well valued properties. Strontium which as trace element is present in the mineral phase of bone is one of wery comonly used for calcium substitution to improve bone strength and even reduce risks of osteoporosis [2, 3, 4]. Strontium hydroxyapatite as bioactive bone cement is used in spinal and bone fracture surgery, in bone replacement, bone fillings and bone adhesives [5].

Despite broad research in hydroxyapatite field still there are some improvements to be done to impart antibacterial capability. To exterminate or at least to minimize the undesirable infection threats, it is necessary to improve hydroxyapatite antibacterial properties. Hydrogen peroxide (H_2O_2) has an antibacterial effect and although it was widely thought that H_2O_2 is very toxic in vivo and must be rapidly eliminated employing several enzymes, also is found in the human body – it is generated by phagocytes to modulate the inflammatory processes [6].

Incorporation of both Sr and peroxide in apatite lattice structure would result by biomaterials having antiseptic and anti – inflammatory properties. There are several ways of synthesis of such materials, for example, treatment at 1000 ^oC temperature which lasted at least two days [7] or annealing treatment which was conducted at 800 ^oC for 2h [8]. Despite the increased research of

hydroxyapatites during last decades, there is still informational lack in basics of peroxyapatite and the most appropriate synthesis routes have still not been developed.

Experimental

Strontium hydroxyapatite (SrHAp) powder was obtained by wet chemical method using two solutions. Solution A consisted from 0.02 mol of $Ca(NO_3)_2$, 0.06 mol of $Sr(NO_3)_2$, and 0.4 mol of NH_3 water solution, but 0.03 mol of $(NH_4)_2HPO_4$ and additive of $(NH_4)_2CO_3$ was used for preparing of solution B. Analytical grade chemicals were dissolved in deionized water and the two solutions mixed, the obtained suspension was stirred for 10 minutes, filtered, washed, and dried at 100 ^oC for 30 minutes.

SrHAp was used as the host powder for peroxide ions to create strontium peroxyapatite. Synthesis of SrPerAp was performed in a closed system - hydrothermal steel pressure vessel (total volume $2.5 \cdot 10^{-5}$ m^3) at temperature diapason from 150 till 110 ^oC, contrary to the higher temperatures used in the previous research works and contrary to notably higher temperatures used by other authors [7, 8, 9]. After loading 0.05 g of SrHAp powder and 4 mL of concentrated H_2O_2 solution in the hydrothermal steel pressure vessel, the hydrothermal pressure system was heated for 1, 3 and 6 hours and afterwards cooled under cool air flow with cooling rate $1,5^o$ per min.

The classical permanganometric redox titration was applied to determine the content of H_2O_2 in peroxyapatite. After dissolving SrPerAp in concentrated perchloric acid and diluting with deionized water, the titration was applied using potassium permanganate solution (0.001 M) until the stoichiometric point was reached. To clarify extent of peroxide decomposition during hydrothermal processing, the same redox titration method was used to determine concentration of residual peroxide solution.

The physico-chemical characteristics were followed by other complementary technique. The obtained powder of SrPerAp was investigated by X-ray diffraction on a D8 Advance diffractometer (Bruker), recorded from 5^o till 60 ^{o} using Cu Kα radiation (λ = 1.54180Å generated at 40 mA and 40 kV).

Results and Discussion

X-Ray Difraction analysis. As it was predicted by lowering the hydrothermal treatment temperature until 110 ^oC, the results of XRD analysis of synthesized powders displayed two types of patterns depending on the heating temperature, Fig. 1. Diffraction peaks of peroxyapatite samples obtained at temperatures 150 and 130 ^oC (samples treated for 3 and 6 hours) are sharp and characteristic of a well-crystallized peroxyapatite, the hydrothermal process treatment has apparently improved the crystallinity of strontium peroxyapatite samples. This shows that the previously developed method of peroxyapatite synthesis is reproducible also at lower temperature range [10]. XRD results indicated that the hydrothermal treatment of the apatite samples at 110 ^oC was insufficient to obtain well-crystallized peroxyapatite although at treatment duration - 6 hours small diffractions peaks started to form but the corresponding pattern of sample treated for 1h is witnessing the similar structure of amorphous SrHAp, Fig.1. The powder color serves as a visual characterizing parameter of successful hydrothermal process. Those samples showing amorphous structure in XRD patterns remained in white color, but SrPerAp samples with crystalline structure changed their coloration to light yellow, what is in a good agreement with other studies [7].

ISBN: 978-1-61804-295-8

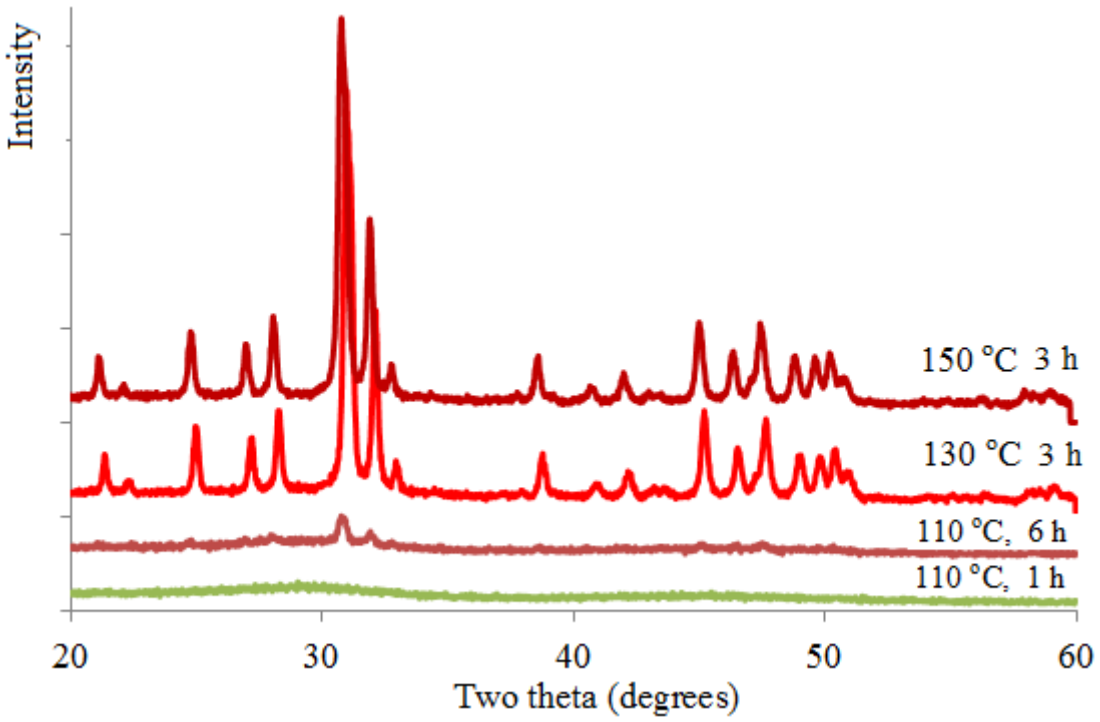

Fig. 1 XRD results of strontium substituted apatite samples after hydrothermal treatment in H_2O_2 medium

Peroxide quantification. A classical redox titration served for the peroxide quantification in obtained strontium peroxyapatite samples, leading to a peroxide content in ranges of 1.0 to 2.9 %. As it can be observed from Fig. 2a, peroxide content varies depending on the hydrothermal processing duration and temperature. Higher values of peroxide content in strontium peroxyapatite were obtained during SrHAp hydrothermal processing at 110 and 130 ^{o}C if duration of process was only 1 hour. But we must admit that theoretical value of peroxide ion weight percent 2.4 % are exceeded in particular samples. It testifies thus not only peroxide incorporation in an apatitic lattice channels occurs but possibly H_2O_2 molecules could be associated to an apatite like water molecules or some other oxygenated species (for example O_2^-) may be present after hydrothermal processing as it was described previously [10]. These results confirmed the presence of peroxide ions in the composition of strontium apatite samples treated in H_2O_2 medium even at 110 ^{o}C.

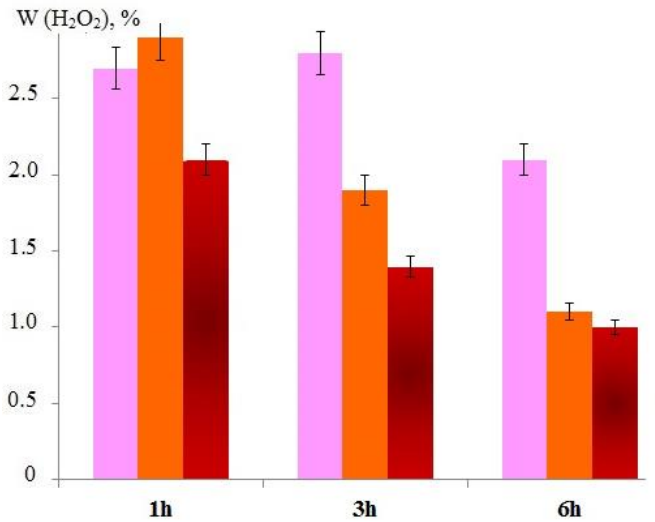

Fig.2a Weight percentage of H_2O_2 after SrHAp treatment at 110, 130 and 150 ^{o}C for 1, 3 and 6 hours.

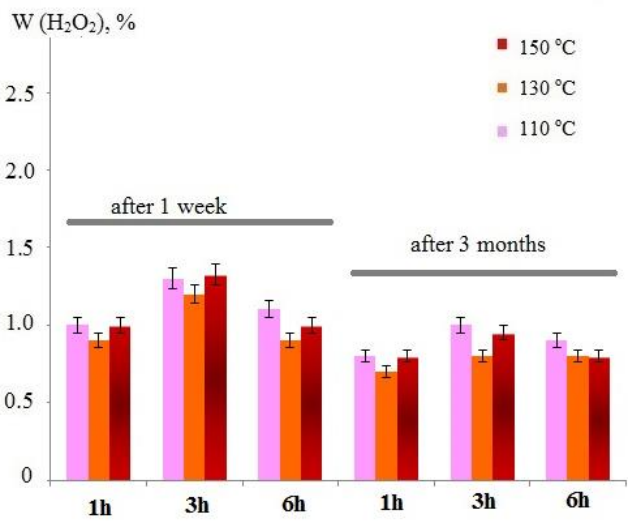

Fig. 2b Weight percentage of H_2O_2 after one week and three months.

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Stability of SrPerAp. Investigation of peroxide content in SrPerAp powders has showed noteworthy changes over time. The highest peroxide concentrations are detected by redox titration just after the synthesis process. Repeated titration already one day after hydrothermal powder treatment indicated reduction in approximately 5-7 % of previously determined peroxide content, the most remarkable decrease (50-60 %, Fig. 2b) occurs after one week of powder storage at 4 ^{o}C. In Fig. 2b we can also observe that minor changes of peroxide content have affected samples treated at higher temperature ranges and with longer processing duration. Peroxide content in SrPerAp powders remain rather stable (0.8 – 0.9 % wt) after three months storage and the total average loss of initially determined peroxide content approach 70 %. Such stable peroxiapatites could be favorable material for implants, which are safe for a living body.

Impact of hydrothermal process. Originally the critical pressure and temperature of the hydrothermal pressure processing was calculated and these results adverted that heating temperature should not reach 180 ^{o}C for safety reasons. Analysis of apatite powder obtained after hydrothermal synthesis process at severe temperatures indicated that the detected peroxide amount increased by lowering the temperature from 170 ^{o}C (previous work [11]) until 110 ^{o}C, but unfortunately the remarkable loss of initially determined peroxide attested week peroxide incorporation in the apatitic lattice. This brought us to the efficiency verification of hydrothermal process therefore after hydrothermal treatment concentrations of residual peroxide solution were determined also by permanganometric titration (molar concentration of $KMnO_4$ was 0.02M). Results testified that used 50 % wt H_2O_2 solution is very well stabilised and increased temperature and pressure during hydrothermal processing leads to poor peroxide decomposition – around 15 % of initial concentrated peroxide that gives approximately 5 mmols O_2. Obtained load of O_2 did not show significant variations depending on hydrothermal processing duration and temperature, exception was 6 hours' process at 150 ^{o}C which gave higher O_2 amount. Regarding above mentioned, the usage of the catalyst containing Mn^{2+} ions was supported. The peroxide decomposition experiments showed that previously achieved 15 % of initial peroxide solution decomposition has been approached during the first minutes of experiment. The usage of catalyst during apatite hydrothermal processing will be developed in future studies.

As it was found out that peroxide decomposition and formation of O_2 is not the only process accountable to peroxyapatite formation, and since the 50 % H_2O_2 solution boiling point is 114 ^{o}C, peroxide gaseous phase may give some contribution.

Conclusion

Modifying strontium hydroxyapatite by hydrothermal processing at 130 – 150 ^{o}C in peroxide medium it is possible to obtain well crystalized strontium peroxyapatite with average peroxide weight percentage 1.7 % (substitution 0.74), at lower temperature – 110 ^{o}C, determined average peroxide content is higher – 2.8 %, but X-Ray Difraction patterns indicate still amorphous structure. Although treated powders with higher detected peroxide content are not stable and within several weeks peroxide content is decreased by 70 %. To achieve complete hydrogen peroxide decomposition during hydrothermal process and more effective peroxide incorporation in apatitic lattice, a catalyst will be used in further work.

Acknowledgement

Support from the ESF project 2013/0028/1DP/1.1.1.2.0/13/APIA/VIAA/054 is gratefully acknowledged.

References

[1] N. Rangavittal, A.R. Landa-ca´ novas, J.M. Gonza´ lez-Calbet, M.Vallet-Regı´. J. Biomed.Mater. Res. 51, 2000, 660–668.

[2] A. Bigi, E. Boanini, C. Capucini, M. Gazzano, Inorganica Chimica Acta. 360, 2007, 1009-1016.

[3] L. Yingguang, Y. Zhuoru, C. Jiang, W. Lianshi, J. of Wuhan University of Technology-Mater. 2008, 475-479.

[4] S.P. Nielsen, Bone, 35, 2004, 583-588.

[5] M.D. Grynpas, E. Hamilton, R. Cheung, Y. Tsouderos, P. Deloffre, M. Hott, P.J. Marie, Bone 18, 1996, 253.

[6] B. Halliwella et. al. FEBS Letters, 486, 2000, 10-13.

[7] J.C. Trombe, G. Montel, J. inorg. nucl. Chem. 40, 1978, 23-26.

[8] H. Zhao, X. Li, J. Wang, S. Qu, J. Weng, X. Zhang, J. Biomed Mater. Res. 52, 2000, 157-163.

[9] P.E. Kazin, M.A. Zykin, R.E. Dinnebier, O.V. MagDysyuk, Y.D. Tretyakov, M. Jansen, Z. Allg. Chem. 638 (2012) 909-919.

[10] A. Osite, K. A. Gross, A.Viksna and R. Poplausks. Mat. Sc. Eng., submitted.

[11] K.A. Gross, A. Jersova, A. Viksna, Key Eng. Mater., 631, 2014, 88.