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Optimization of Non-Conventional Sintering of Hydroxyapatite for Immobilization of Radioiodine

Muhmood ul Hassan, Ho Jin Ryu*
Department of Nuclear and Quantum Engineering, KAIST, Yuseong, Daejeon 305-701, Korea
Corresponding author: hojinryu@kaist.ac.kr

1. Introduction

The production and immobilization of volatile radionuclides like radioiodine is one of the major issues associated with acceptance and commercialization of used nuclear fuel reprocessing as well as vitrification process. Therefore a viable solution which can not only effectively immobilize this kind of radionuclide as well as has good durability during long term disposals is required. In case of radioiodine which has a volatilization temperature of 500^{O}C high temperature immobilization routes like vitrification are in effective. Very long half-life (~1.6 x 10^7 years) and high mobility of the radioiodine makes requires more attention for its handling and immobilization among other ILW volatile fission by products. The substitution of actinides as well as fission products into crystalline phases of different mineral analogs like apatites, zeolites, zirconolite, ceramicrete etc. is being thoroughly investigated in order to find low temperature and stable immobilization routes[1]. In this regard the selection of phosphates as host matrices for immobilization of radioiodine is based on insoluble properties of the phosphates into ground water as well as high radiation and chemical stability[1].

In order to show the capabilities of hydroxyapatite structures to incorporate radioiodine, iodide substituted and iodate replaced calcium hydroxyapatite has already been synthesized and reported elsewhere[4,5]. However, the synthesized apatite has high exchange surface because of the high porosity which requires further treatment i.e. sintering to produce dense matrices.

In this study we have successfully sintered the synthesized HAP at an extraordinary low temperature of 200 ^{O}C by applying a uniaxial pressure of 500 MPa in short holding time of 10 minutes and achieved a relative densities > 90% as first step towards the sintering of iodate substituted hydroxyapatite.

2. Methods and Results

2.1 Apatite Synthesis

wet precipitation method as described in reference [4] has been used to synthesize crystalline apatite. Anionic and cationic solutions were prepared by dissolving each di-ammonium hydrogen phosphate {$(NH_4)_2HPO_4$} and calcium nitrate {$Ca(NO_3)_2{\cdot}4H_2O$} in 100ml of double deionized water respectively. The pH of the solutions were adjusted at 10.5 by using concentrated ammonia {$NH_4(OH)_2$}. All used materials were of reagent grade. Then anionic solution was mixed with cationic solution dropwise during 60 minute under continuous stirring at the rate of 200RPM and temperature was maintained at 30^{O}C. The pH of solution was continuously monitored by using digital pH meter and was maintained at 10.5 throughout the synthesis period by dropwise addition of concentrated ammonia. At the end of synthesis, precipitate was left inside the parent solution for 12 hrs at 30^{O}C for ageing. After 12hrs, suspension was filtered and thoroughly washed with double deionized water. Finally the filtrate was dried overnight at temperature 50^{O}C by using vacuum oven.

2.2 Powder Characterization

XRD pattern of the apatite powder was obtained by using SmartLab, RIGAKU, high resolution powder X-ray diffractometer and the 2Θ range was between 20 and 60◦ (Fig.1.).

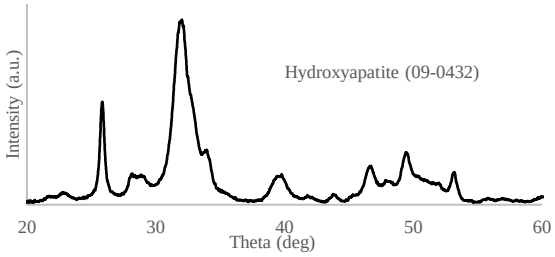

Fig. 1. XRD patterns of the synthesized dried calcium hydroxyapatite showing no other phase except apatite.

FTIR of the synthesized powder revealed the presence of small amounts of carbonates which was obvious as the synthesis was carried out in air environment. All other vibrations were related to the apatite functional groups (Fig.2.).

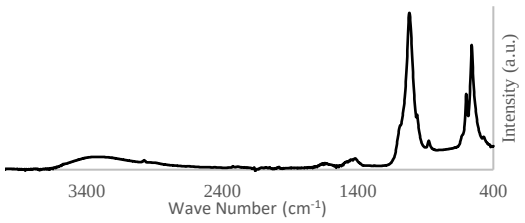

Fig. 2. FTIR spectra of the synthesized hydroxyapatite.

TEM images of the dried powder showed rice like morphology (Fig.3).

Ca/P ratio was measured from the ICP-OES results of the synthesized powder and results revealed stoichiometric nature of the synthesized apatite powder. Surface area was measured as 112.35 m^2/g by using BET method. The measured density of synthesized powder was 2.70 g/cm^3 whereas the relative densities has been measured by using the theoretical density of the apatite powder i.e. 3.16 g/cm^3.

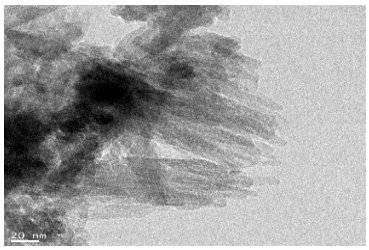

Fig.3. TEM image of the hydroxyapatite powder showing the nano rod like morphology of the synthesized powder.

2.3 Sintering of Apatite

The sintering of apatite powder was carried out by using uniaxial press. 0.5 gm of apatite powder was poured in steel mold having17mm internal diameter. The mold was covered with a heating band and placed in the uniaxial press. A pressure of 500 MPa was determined as the optimized pressure to achieve the highest sintering density. Heating band was used as a sources of heat and a temperature controller was used to control the set temperature and heating rate.

A temperature of 200 ^{O}C gave maximum sintered density for a holding time of 10 minutes. The densities achieved for different applied temperatures, pressures, and holding times are as shown in the figures 4-A, B, C.

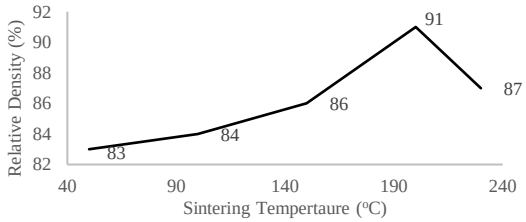

Fig.4-A. Effect of sintering temperature on density.

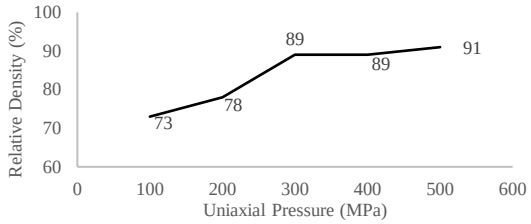

Fig.4-B. Effect of applied pressure on the density under constant temperature conditions.

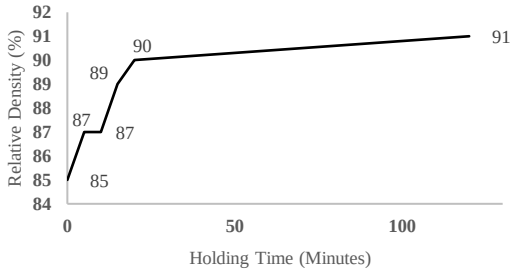

Fig.4-C. Effect of holding time on density under constant temperature and pressure conditions

2.4 Vickers Hardness

Hardness of sintered samples was measured by using the Vickers testing procedure. The load of 500 gf was applied for dwell time of 10 sec. An average value of 2.46 GPa of Vickers hardness was measured whereas the yield strength was calculated as 0.82 GPa.

3. Conclusion

In this work, ultra-low temperature sintering of apatite by using non-conventional sintering technique was demonstrated first time. We have investigated that the morphology as well as bonded water both are vital to achieve this ultra-low temperature sintering. We have optimized sintering conditions to achieve the highest relative density as well as good mechanical properties. This leads to our final goal of development of an ultralow temperature sintered matrices for the immobilization of I-129 for long term geological disposal. Further work is still in progress to study the durability of the sintered matrices to further ensure its suitability to be used as immobilization matrices.

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