Katıhal Metodu ile Deniz Kestanesi Kabuğundan Hazırlanan Whitlockite Biyoseramik Ön Malzemesinin Karakterizasyonu

Characterization of Whitlockite Bioceramic Precursor Prepared from Sea Urchin Skeleton by Solid State Method

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***Özetçe*—Deniz canlıları kimyasal yapılarının genellikle yüksek oranda saf kalsiyum karbonattan ve az miktarda yabancı maddeden oluşmalarından dolayı biyomedikal uygulamalarda kullanılmak üzere sentezlenecek olan kalsiyum fosfat bileşiklerinin elde edilmesinde alternatif bir kaynak olarak kullanılmaktadır. Bu çalışmanın amacı, katı hal yöntemi ile deniz kestanesi kabuğu ve yine bundan elde edilen CaO kullanılarak whitlockite biyoseramik toz hammaddesi üretilebilmesinin araştırılmasıdır. Çalışma sonucunda elde edilen whitlockitın morfolojisi ve yapısı X-Işını Difraksiyonu (XRD), Kızılötesi (FTIR) ve Elektron mikroskobu (SEM) kullanılarak belirlenmiş ve sonuçlar deniz kestanesi kabuğunun direk kullanılması ve yine kabuktan elde edilen kalsiyum oksitin whitlockite eldesinde kalsiyum kaynağı olarak kullanılabileceğini ve mekanik öğütme yardımlı katı hal sentez yöntemi ile bu bileşiğin elde edilebileceğini göstermiştir.**

Anahtar Kelimeler — Whitlockite, Tricalcium phosphate, Biyoseramik, Deniz kestanesi kabuğu, katıhal sentez.

***Abstract*— Marine species have been used to obtain calcium phosphate compounds as alternative sources for biomedical application due to their chemical structures which are generally composed of pure calcium carbonate with small amount of impurities. The aim of the present study is to be synthesized of whitlockite bioceramic powder precursor using sea urchin skeleton by solid state method. In a synthesis procedure, CaO which was obtained from sea urchin skeleton and directly sea urchin skeleton were used as starting materials. The morphologies and structures of the obtained whitlockite which were determined by XRD, FTIR and SEM indicated that the calcium carbonate and calcium oxide from sea urchin skeleton could be used as a calcium precursor on the conversion process of whitlockite which could be successfully synthesized by solid state method with helping the mechanical attrition.**

Keywords — Whitlockite, Tricalcium phosphate, Bioceramic, Sea urchin skeleton, solid state synthesis.

I. INTRODUCTION

Calcium phosphates-based bioceramics are obtained in various forms and widely used as biomedical implant materials due to excellent biocompatibility with living body and bioactivity[1]. For example, bioceramics made of tricalcium phosphate can be used as bone grafts. Whitlockite has nearly same structure with tricalcium phosphate, meaning that it may be used for same applications. But it contains little amount of magnesium which creates the difference. However magnesium ions may very useful to promote bone cell adhesion, differentiation and proliferation [2].

Calcium phosphate powder compounds as bioceramic precursors can be synthesized using calcium oxide or hidroxide with potasium source as starting chemcials by various synthesis routes like precipitation, hydrothermal, hydrolysis, solid-state reactions and sol-gel techniques that synthesis routes significantly affect the physical and structural properties which have an important for specific applications[3].

Marine species are generally composed of pure calcium carbonate with small amount of impurities and readily available and abundant. However they have yet to be enough investigated for their possible applications or potentials as a source of value-added components. Sea urchin skeleton is one of them and can be easily found in the coast of our country. The aim of the present study was to synthesis of the whitlockite using directly sea urchin skeleton or CaO which was obtained from it by solid state synthesis method. In addition, a comparative study was carried out to see the effect of starting materials and mechanical attrition on the structure of whitlockite.

II. MATERIALS AND METHODS

The conversion of the sea urchin skeleton (collected from Foca in Izmir, Turkiye) to whitlockite were carried out by solid state method using two different calcium sources: the first one was directly sea urchin skeleton (coded as whitlockite I) and a second one was CaO (coded as whitlockite II) which was obtained from the sea urchin skeleton by calcination process at 1050 °C for 2 hours. In order to synthesize whitlockite, the experimental procedure was based on the study conducted by Ahmed et al. [4]. The requisite amount of sea urchin skeleton powder and (NH_4) H_2PO_4 were mixed (Ca/P ratio at 1.6) and then ground for about 8 hrs using planetary ball mill. After the milling procedure, the powders were sintered at 1050° for 3 hrs. Same experimental condition was followed for CaO as a starting compounds.

X-ray powder diffraction (XRD) was used to identify the phase compositions and crystallinity of the samples and the patterns were obtained using Rigaku Miniflex 600 Diffractometer with Cu Kα (40 kV, 15 mA, k = 1.54050 Å). The functional groups and the morphology of the samples were determined by Fourier transform infrared (FTIR, Perkin Elmer, Spectrum One) and LeO EVO 40 scanning electron microscope, respectively.

III. RESULTS AND DISCUSSION

XRD patterns of the raw sea urchin skeleton, CaO (obtained from sea urchin skeleton) and the synthesis whitlockite powders are depicted in Figure 1. The XRD patterns belonging to the sea urchin skeleton indicates that the main structure is magnesium calcium carbonate, $(Mg_{0.06}Ca_{0.94})(CO_3)$ since the all patterns match well with the powder diffraction data reported in JCPDS Card No: 01-089-1306. The XRD patterns belonging to calcinated sea urchin skeleton shows that the main structure is CaO (JCPDS-PDF 48-1467) with some small diffraction lines from MgO (JCPDS-PDF 45-0946). After a successive and intensive milling process of the sea urchin skeleton with (NH_4) H_2PO_4 and CaO with (NH_4) H_2PO_4 , and by heating the mixture powders at 1050° for 3 hrs, new phases, whitlockite, were seen. It means that the whitlockite can be successfully synthesized from the sea urchin skeleton by the solid state method. Considering the chemical structure of bioceramic materials in the fields of orthopaedics and dentistry, the ions of magnesium inside the calcium phosphate based bioceramic precursors can positively influence the biological performance the ceramics since magnesium increase in mechanical properties of apatite [1].

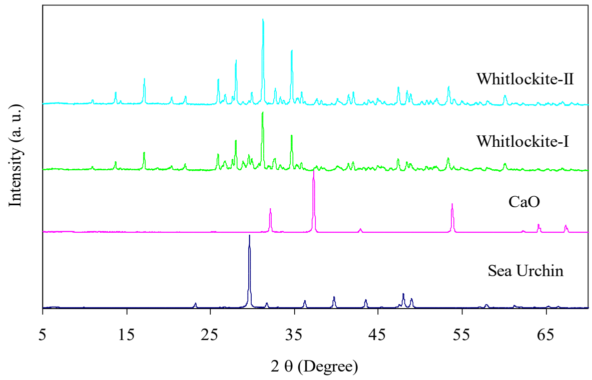

Figure 1. X-ray diffractograms of powder samples. Sea urchin skeleton, skeleton calcinated at 1050 °C for 2 h (named CaO), the whitlockite I synthesized using the sea urchin skeleton and the whitlockite II synthesized using the calcinated CaO.

The FTIR spectrum of the whitlocikte indicates the characteristic peaks corresponding to the structure of PO_4 vibrations: 1026 and 927,07 cm^{-1} are attributed to PO_4 ν_3 and PO_4 ν_1, respectively[6].

SEM micrographs for the sea urchin skeleton (a), CaO (b) and the whitlockite I (c) and whitlockite II (b) are depicted in Figure 2. The chemical analysis proved that the sea urchin skeleton mainly composed of calcium carbonate and SEM image shows the regular $CaCO_3$ structure. Non uniform morphology and irregular particle shapes may be associated with a higher hardness of the skeleton. The calcinated sea urchin skeleton (CaO in Figure 2. b) shows regular particle shapes with agglomeration structure demonstrating high temperature calcination procedure. SEM analysis indicates that the whitlockite consists of plate-like crystals and nearly same morphology are seen for both the whitlockite I and whitlockite II. Like XRD results, it means that the whitlockite can be synthesized using directly sea urchin skeleton and CaO calcinated from the sea urchin skeleton by solid state method. In addition, the recorded EDX spectra (not given in text) of the synthesized whitlockite bioceramic precursors showed the presence of the elements Ca, Mg, P and O in all the two obtained samples.

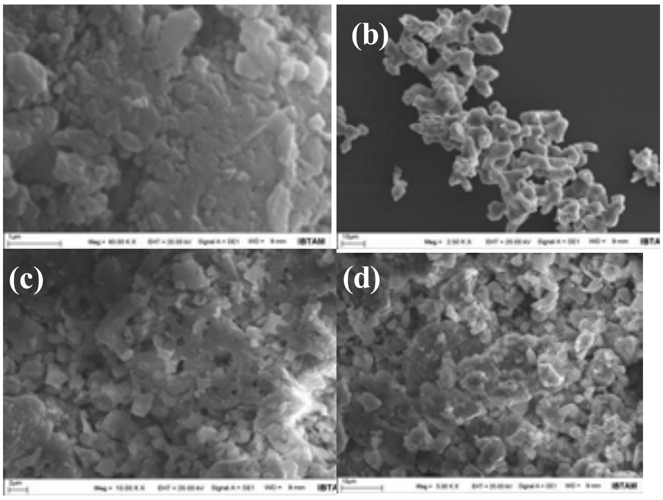

Figure 2. SEM images of sea urchin skeleton (a), CaO (b), whitlockite I (c) and whitlockite II (d)

IV. CONCLUSION

In the light of the experimental results, the following conclusions were obtained:

1. Sea urchin skeleton could be chosen as a starting materials for calcium source to production of calcium phosphate bioceramic precursor.

2. Characterization studies indicated that the whitlockite could be succefully synthesized by simple solid state methods with the help of mechanical attrition using plenatary ball mill.

3. Comparasion of the characterization studies of the whitlockite I and whitlockite II indicated that the same chemical structures were obtained for both, meaing that the whitlockite could be obtained directly using the raw sea urchin skeleton without any further treatment like calcination process to obtain CaO. This would be very advantages economicaly.

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KAYNAKÇA

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