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M.A.TEMIRBAYEV[*1], *З.A.MANSUROV*[2], *CH.B. DAULBAYEV*[2], *K.P.DOSMATOVA*[1]

[1]Kazakh medical university of continuing medical education
[2]RSE «Institute of combustion problems», Almaty

NANOCRYSTALLIC HYDROXYAPATITE FROM BIOLOGICAL MATERIAL FOR PRACTICAL HEALTH CARE

SUMMARY

Human and animal bone tissue is composed of the protein and mineral components such as calcium hydroxyapatite. Chemically synthesized hydroxyapatite, a highly dense crystalline material is used to fill bone defects during surgical treatment in traumatology and orthopedics, dentistry, and maxillofacial surgery. Nano crystalline form of hydroxyapatite calcium has another organizational structure with other methods of hydroxyapatite synthesis, a method of applying various implants to the surface, biocompatibility, toxicological and allergenic manifestations, mainly used for coating implants, dental cements and medical pastes due to its high bioactivity and the possibility of creating composite materials on its basis [1]. This paper describes the process of synthesis of hydroxyapatite with the method of calcination using the egg shell of birds as a biological raw material. Electron microscopy studies showed that the resulting powder is a single-phase, thermally stable up to 900 ° C and morphologically homogeneous. The globules are composed of nano crystals with average size of around 50 nm.

Key words: egg shell, nano crystalline hydroxyapatite

According to the World Health Organization, the development of the technogenic sphere severely damages the human health. In particular, the bone tissue is one of the most vulnerable structures of the body. It is well known that human and animal bone tissue consists of a protein matrix, individual for every biological individual, and a mineral component composed of an inorganic calcium and phosphorus compound, calcium hydroxyapatite The use of chemically synthesized hydroxyapatite to fill bone defects during surgical treatment started in the late 70s of the XX century and is widely used at the present. This material is widely used in the modern traumatology, orthopedics, dentistry and maxillofacial surgery. Calcium hydroxyapatite, currently used to fill bone tissue defects, is basically a dense, highly crystalline material that withstands significant mechanical stresses by introducing hardening additives. Upon creating implants based on hydroxyapatite, researchers studied deeply methods of hydroxyapatite synthesis and its application to different surfaces of various implants, biocompatibility, toxicological and allergenic manifestations, but its structural organization was poorly investigated. For coating implants, dental cements and medical pastes, the nano crystalline form of hydroxyapatite is used due to its high bioactivity and the possibility of creating composite materials on its base. [1]

Experimental part

HAP was synthesized by calcination using a biological source - the egg shell of birds. Electron microscopy studies showed that the resulting powder is a single-phase, thermally stable (up to 900 ° C), morphologically homogeneous and is composed of 4-5 μm globules, which in turn are consist of nanocrystals of the size of around 50 nm.

A distinctive feature of our technique is obtaining of one of the basic components of the reaction - calcium oxide (CaO) during the processing of the eggshell. The egg shell is used as a main material because it is composed of calcite - CaCO3 for 95%. The remaining is an organic matter - several layers of interlacing protein fibers and various mineral salts (<1%), placed similar to calcite, on the surface of these protein fibers. On heating, CaCO3 decomposes into CaO and CO2:

$$CaCO_3 \rightarrow CaO + CO_2 \ (T = 900\,°C) \qquad (1)$$

Prepared shell, containing CaCO3, was washed and calcined at 900 ° C. After 30 minutes, the color of the egg shell turned into black, and upon further 3 hours it became white. The color change showed that most of the organic materials were burned. The powders were crushed in an agate mortar followed by an exothermic reaction with phosphoric acid. Further details of the mixing procedure and powder preparation are presented in Table 1.

Table 1. Calcination of the eggshell

Samples	Eggshell, %	H_3PO_4, %	Ball mill, hours	Parameters	
				T°C	τ, hours
A	50	50	10	-	-
AS	50	50	10	900	2

*mtemirbayev@mail.ru

After calcination at 900 ° C for 3 hours, the resulting CaO oxide forms Ca (OH) 2 after reacting with the surrounding atmospheric air.

$$CaO + (air) \rightarrow Ca(OH)_2 \quad (2)$$

The obtained calcium hydroxide Ca (OH) 2 was titrated at the room temperature with a solution of orthophosphoric acid H3PO4 (70%) to produce hydroxyapatite.

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)(OH)_2 + 18H_2O \quad (3)$$

Upon that, the obtained hydroxyapatite was grounded in a ball mill. The samples were dried at 400 ° C for an hour for further analysis. It should be noted that the entire process of hydroxyapatite preparation, depending on the concentration of the initial reagents, can take different time, and the process does not require special conditions or additional inhibitors. [4]

Results and discussion

Characteristics of the obtained samples of HAP were studied by using a complex of flow and spectral methods. Thus, impurities of the initial shell were studied with X-ray phase analysis (XRD) and electron microscopy.

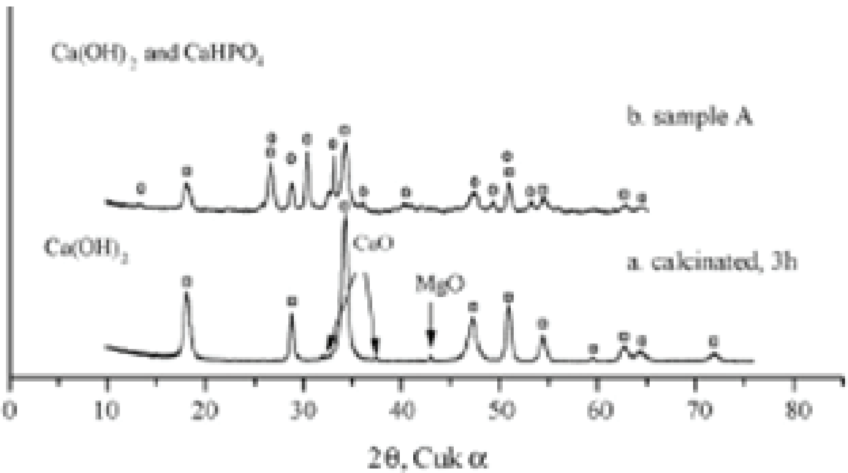

Figure 1. X-ray diffraction patterns of powder samples. (a) shell calcite at 900 ° C in 3 hours and reacting with air, (b) Ca (OH) 2 product with phosphoric acid [3]

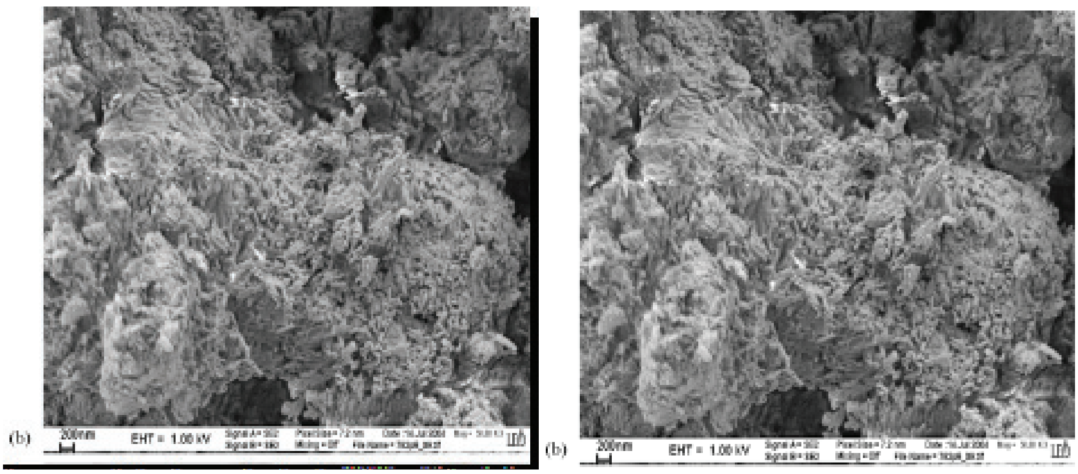

Figure 2. Electron microscope images of (a) shell calcite at 900 ° C after 3 hours, (b) the resulting product of Ca (OH) 2 with phosphoric acid. [3]

In the future, it is planned to use electrospinning to apply hydroxyapatite on to the surface of a polymer base. Electrospinning is a method of obtaining fine fibers using an electric field. Electrospinning is a well-known method for creating nano and micro polymer fibers. Synthesis of hybrid ceramic polymer nanofibers using electrospinning is a major breakthrough in the field of biotechnology associated with nanoproduction. A polymer solution represents the classical starting composition for the production of the fiber.

A scheme for the installation of conventional electrospinning is provided below [3].

*mtemirbayev@mail.ru

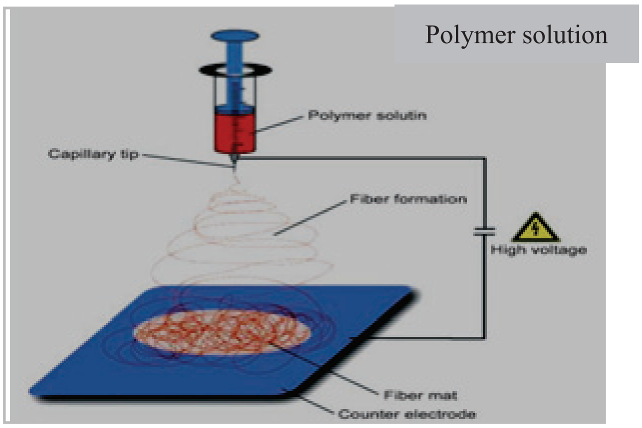

Figure 3. Standard Electrospinning Unit

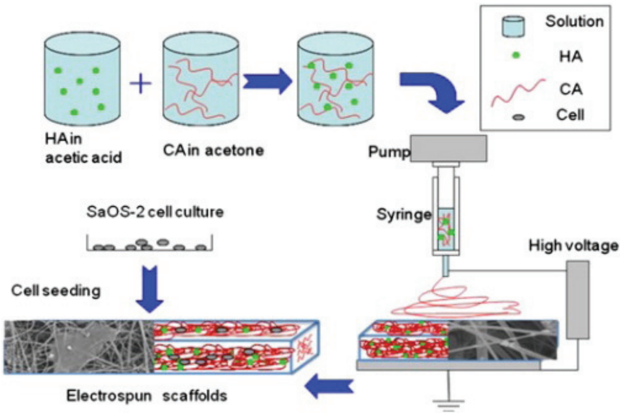

Figure 4. Electrospun principles

The principle of electrospinning device is simple: a polymer solution is mechanically squeezed out of a syringe. From the tip of this syringe needle, on which additional high voltage is applied, a stream of the solution emerges. Then, as the stream progresses, the solvent is evaporated, and the remaining material, which is a forming fiber, is collected at the second high voltage electrode.

Figure 4 shows the 3D synthesis of porous fibrous frameworks. Nano-HA (nano-hydroxyapatite) powder was synthesized from the raw materials. The resulting n-HA powder was added to acetic acid, forming 9.38% w / v solution. This solution was then mixed with cellulose acetate (AC) solution and this mixture was further dissolved in acetone to form a 15% w / v composition. The mixed solution (71-29% acetone / acetic acid) was introduced into a standard vertical electrospinning unit and electrospun was conducted under the following conditions: flow rate 9.6 ml / h, voltage 19 kV and distance 10 cm from the needle to the manifold [3,7-8].

Conclusion

Thus, based on the results obtained, the following conclusions can be drawn:

1. Hydroxyapatite was experimentally synthesized from the egg shell of birds.
2. Phase composition of the obtained hydroxyapatite was studied.
3. Using electrospinning method on hydroxyapatite base will allow obtaining a material for effective replacement and regeneration of the bone tissue.

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*mtemirbayev@mail.ru

АННОТАЦИЯ

Костная ткань человека и животных состоит из белковой материи и минеральной составляющей, гидроксиапатита кальция. Химически синтезированный гидроксиапатит, плотный высоко кристаллический материал, используется давно для заполнения дефектов кости в процессе хирургического лечения в современной травматологии и ортопедии, стоматологии, челюстно-лицевой хирургии. Нано кристаллическая форма гидроксиапатита кальция имеет другую структурную организацию с другими методами синтеза гидроксиапатита, способом нанесения на поверхность различных имплантатов, биосовместимостью, токсикологическими и аллергенными проявлениями, в основном используется для покрытий имплантатов, зубных цементов и медицинских паст из-за высокой биоактивности данного соединения и возможностью создания композиционных материалов на его основе. [1]

В данной работе подробно описан процесс синтеза гидроксиапатита методом кальцинирования с использованием биологического источника — яичной скорлупы птиц. Исследования, проведенные методами электронной микроскопии, показали, что полученный порошкообразный материал в виде глобул микронных размеров (4—5 μm) является однофазным, термически стабильным до 900° С, морфологически однородным. Глобулы состоят из нано кристаллов со средними размерами порядка 50 нм.

Ключевые слова: яичная скорлупа, нано кристаллический гидроксиапатит

ТҮЙІНДІ

Адам мен жануарлардың сүйек тіні кальций гидроксиапатитін құрайтын ақуыз материядан және минералдан тұрады. Химиялық синтезделген гидроксиапатит, жоғары тығыздықты кристалл материал заманауи травматологияда, ортопедия, стоматологияда, жақ-бет хирургиясындағы хирургиялық емдеу үдерісіне сүйек ақауларын толтыру үшін бұрыннан қолданылады. Кальций гидроксиапатитінің нанокристалдық түрі басқа гидроксиапатит синтезі әдісімен басқаша құрылымдық ұйымы бар, биоүйлесімділігі, токсикологиялық және аллергенді көрсетілімі бар әртүрлі имплантаттарды бетіне жағу тәсілімен, негізінен аталған қосылыстың жоғары биобелсенділігі және соның негізінде композициялық материалдарды құру мүмкіндігіне бола имплантаттарды, тіс цементтері мен медициналық пасталарды жабу үшін қолданылады [1].

Осы жұмыста биологиялық негіз — құстар жұмыртқасының қабығын пайдалана отырып, кальцийлендіру әдісімен гидроксиапатит синтезі үдерісі егжей-тегжейлі сипатталған.

Электронды микроскопия әдісімен жүргізілген зерттеулер алынған микронды мөлшері (4-5 μm) болатын глобул түріндегі ұнтақ тәрізді материалдың бір фазалы, 900° С дейін термиялық тұрақты, морфологиялық біртекті болып табылатынын көрсетті. Глобулдар орташа мөлшері 50 нм болатын нанокристалдардан тұрады.

Кілт сөздер: жұмыртқа қабығы, нанокристалды гидроксиапатит

*mtemirbayev@mail.ru