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HYDROTHERMAL SYNTHESIS OF ZIRCONIA NANO-POWDERS AND FILMS

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The synthesis of nano-powders was accomplished using different physical, mechanical and chemical methods. Hydrothermal processes have been recently reported as a very attractive route in the synthesis of both zirconia powders and films. The present paper presents some aspects of the microstructural evolution of zirconia nanomaterials obtained via hydrothermal process starting from soluble peroxide precursors.

Key words: *nano-powders, hydrothermal process, hydroxiapatite*

Hidrotermička sinteza cirkonijevih nanoprahova i tankih prevlaka. Sinteza nanoprahova izvršena je uporabom raznih fizičkih, mehaničkih i kemijskih metoda. Od nedavno se o hidrotermičkom procesu govori kao o vrlo atraktivnom načinu sinteze cirkonijevog praha i tanke prevlake. Ovaj rad predstavlja neke aspekte mikrostrukturalne evolucije cirkonijevih materijala dobivene hidrotermičkim procesom koji počinje s topljivim početnim peroksidnim materijalom.

Ključne riječi: *nanoprahovi, hidrotermički proces, hidroksiapatit*

INTRODUCTION

During the last year many researches have been devoted to develop and improve the properties of hydroxiapatite (HAP) like bioeconomic materials. HAP based implants present important advantages such as: high biocompatibility, bioactivity and less influence on biodegradation [1]. However, their utilisation is limited by the brittleness and the fracture toughness [2].

Different materials in the form of powders, whiskers or fibers were proposed to be dispersed in HAP matrix. The principal syntheses of nano-powders are in present canalized to the creation of non-conventional processes: colloidal sol-gel or hydrothermal, because these processes allow the stoichiometric control to obtain the products purity and morphology control.

EXPERIMENTAL AND DISCUSSIONS

All the experimental studies were performed in the Institute for Non-ferrous and Rare Metals, Research Department, Ceramic Laboratory, Bucharest.

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Raw materials

Raw materials used:
- $Ca(NO_3)_2$*$4H_2O$ p. a.;
- $NH_4H_2PO_4$ p. a. Merck;
- NH_3 25 % pa;
- solution of $Zr(NO_3)_4$ prepared in the laboratory of IMNR-SA;
- distilled water.

The description of the experimental laboratory device

The experimental laboratory device is consist of:
- thermorezistant glass vessels with different volumes;
- a mechanical stirrer with electronic device for adjusting the speed type AF2;
- a pH-meter with digital display type pH-100;
- ceramic filtering funnels type Buchner;
- laboratory autoclaves manufactured in IMNR, made from a steel resistance cylinder and an interior Teflon reaction recipient, with the capacity of 250 ml and 1500 ml. The lid was sealed on the Teflon trimming with the help of six screws symmetrically disposed on the edge of the lid;
- a laboratory oven for drying the samples;
- an automatic micro-burette type Radelkis.

The pictures of the laboratory device are presented in Figure 1. and Figure 2.

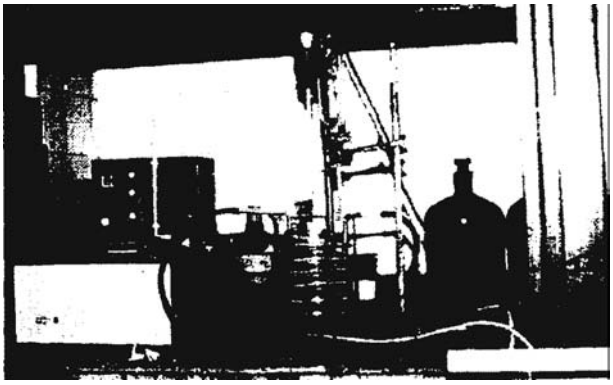

Figure 1. **Laboratory synthesis plant for powders**
Slika 1. **Pogon za laboratorijsku sintezu prahova**

Figure 2. **The filtering system**
Slika 2. **Sustav filtriranja**

Hydrothermal synthesis of HAP

On the basis of experimental results, the hydrothermal synthesis of hydroxyapatite using as raw materials tetra-hydrated calcium ammonia, di-acid ammonium phosphate and 25 % ammonia solution was performed. Determined of calcium nitrate and di-acid ammonium phosphate were solved in distilled water. Molar ratio was Ca : P = 1.67.

Given volumes of these solutions were then stirred in NH_4OH medium at controlled pH values. After this the products were moved in Teflon containers of the autoclaves for the hydrothermal synthesis. After the synthesis the samples were filtered and the precipitates washed in three steps. The mother liquors and the washing waters were chemically analyzed to determine the content of Ca, P, $NH_4(+)$, $NO_3(-)$ left in the solutions.

After drying, the precipitates, were analyzed by X-ray diffraction and scanning electron microscopy.

In Table 1. the synthesis conditions and the results obtained from the complex chemical analysis are shown schematically, and in the Figure 3. the flow chart diagram for the hydrotherrnal synthesis is presented.

The X-ray diffraction patterns of the HAP samples obtained by a hydrothermal procedure in different reaction condition presented in phase analysis the presence of hydroxyapatite as major phase with crystallite sizes of about 1 - 2 μm.

The crystallinity degree is influenced by the synthesis time and temperature. At temperatures of 150 - 200 °C, and the synthesis time of 3h the samples are well crystallized, and the sizes of the crystallite are greater.

Table 1. **Reaction conditions and some experimental results for the HAP hydrothermal synthesis**
Tablica 1. **Uvjeti reakcije i neki eksperimentalni rezultati za HAP hidrotetmičku analizu**

Sample	1		2		3		4		5		6	
Temp. [°C]	21	100	21	100	21	150	21	150	21	200	21	200
Time [hours]	0	2	0	3	0	2	0	3	0	2	0	3
pH initial	9.5	—	9.5	—	9.3	—	9.4	—	9.4	—	9.5	—
Ca initial [g]	0.4186	—	0.4186	—	0.4186	—	0.4186	—	0.4186	—	0.4186	—
P initial [g]	0.22	—	0.22	—	0.22	—	0.22	—	0.22	—	0.22	—
$NH_4(+)$ initial [g]	0.128	—	0.128	—	0.128	—	0.128	—	0.128	—	0.128	—
NH_3 initial [g]	0.452	—	0.452	—	0.452	—	0.452	—	0.452	—	0.452	—
Vol.Mo th. liquor [ml]	—	150	—	210	—	140	—	213	—	145	—	180
pH Mo th. liquor	—	8.86	—	9.08	—	8.94	—	9.17	—	8.93	—	9.2
Ca [g] in Mo. liq.	—	0.0003	—	0.00042	—	0.00028	—	0.00053	—	0.00026	—	0.000486
P [g] in Mo. liq.	—	0.01395	—	0.01806	—	0.0168	—	0.0193	—	0.0159	—	0.0198
$NH_4(+)$ [g] in Mo. liq.	—	0.582	—	0.735	—	0.49	—	0.643	—	0.452	—	0.66
$NO_3(-)$ [g] in Mo. liq.	—	3.86	—	4.13	—	2.92	—	3.26	—	3.04	—	9.2
Ca pp [g]	—	0.4183	—	0.4182	—	0.4183	—	0.4181	—	0.4183	—	0.4181
P pp [g]	—	0.20605	—	0.20194	—	0.2032	—	0.2007	—	0.2041	—	0.2002

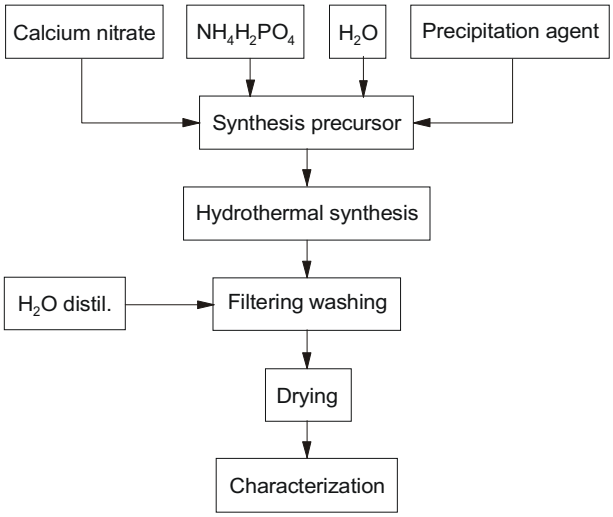

Figure 3. **Theoretical technological draw of hydroxyapatite synthesis**
Slika 3. **Tehnološka shema teoretskog prikaza sinteze hidroksiapatita**

In Figure 4., 5. and 6. the optical microscopies for HAP at different temperatures and different times is presented.

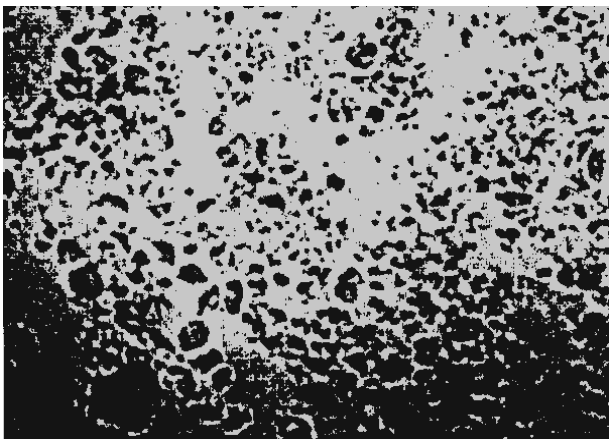

Figure 4. **Optical Microscopies for Hydroxyapatite 200 °/2h**
Slika 4. **Mikroskopski prikaz hidroksiapatita, 200 °/2h**

Determination of the solubility curves for systems Ca(+2)-$NH_4H_2PO_4$-NH_4OH-H_2O and Ca(+2)-$NH_4H_2PO_4$-$Zr(NO_3)_4$-NH_4OH-H_2O

The calcium nitrate tetra-hydrated analytically weighted was dissolved in distilled water, filtered and chemically analyzed for the control of the Ca concentration. The solution of zirconium nitrate prepared in the IMNR laboratory was also chemically analyzed for the control of the Zr concentration and for the free acidity.

A diluted solution of ammonia in water was prepared, chemically analyzed for the determination of the ion $NH_4(+)$ concentration.

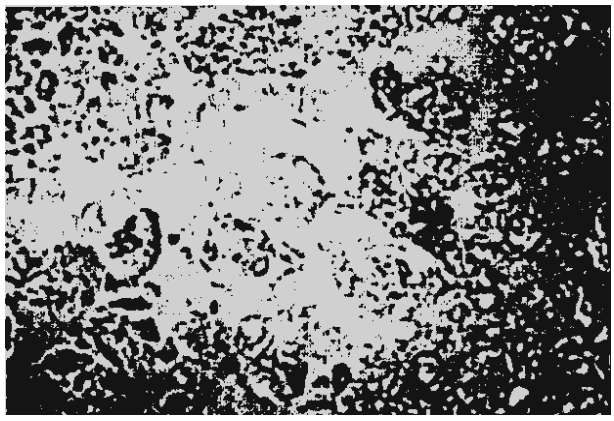

Figure 5. **Optical Microscopies for Hydroxyapatite 100 °/3h**
Slika 5. **Mikroskopski prikaz hidroksiapatita, 100 °/3h**

The experiments were performed with very diluted solutions to be situated in the domain of the ideal solutions.

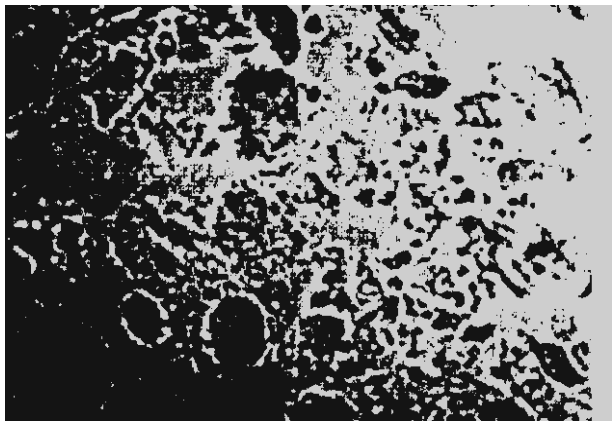

Figure 6. **Optical Microscopies for Hydroxyapatite 150 °/2h**
Slika 6. **Mikroskopski prikaz hidroksiapatita, 150 °/2h**

Given volumes of these solutions plus a quantity of diacid ammonium phosphate weighted on the analytical balance were then titrated with diluted solution of ammonia.

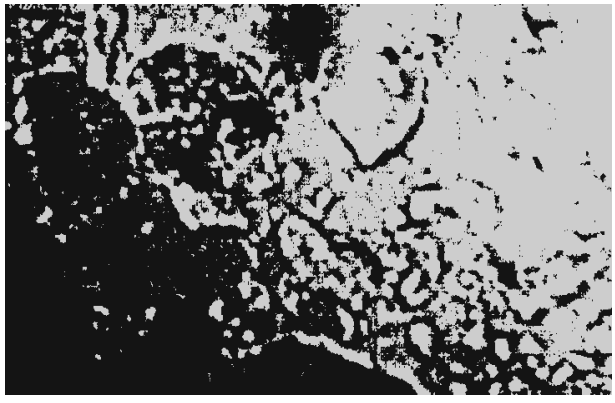

Figure 7. **Optical Microscopies for Hydroxyapatite 100 °/2h**
Slika 7. **Mikroskopski prikaz hidroksaipatita, 100 °/2h**

The variation of pH as a function of added precipitation agent and the precipitated quantity obtained were determined. The experiments took place at room temperature.

The solutions and the precipitates obtained were chemically analyzed for the determination of the Ca, P, Zr content [3].

CONCLUSIONS

The hydrothermal process has been chosen because it has some advantages like:

- the synthesized powders are well crystallized and as a consequence the sintering temp is lower than in classical procedures;
- it is easy to control the powder composition;
- with this procedure also whiskers of HAP can be obtained with superior properties compared with pure hydroxyapatite;
- the pressurized autoclaves used in hydrothermal synthesis can be provided with elect and can be attached to an Potentiostat/Galvanostat. In this way the controlled depositions on some substrates can be obtained;
- its an ecological friendly procedure.

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