EFRE 2020

A new method for the synthesis of coatings of HA-gelatin on titanium

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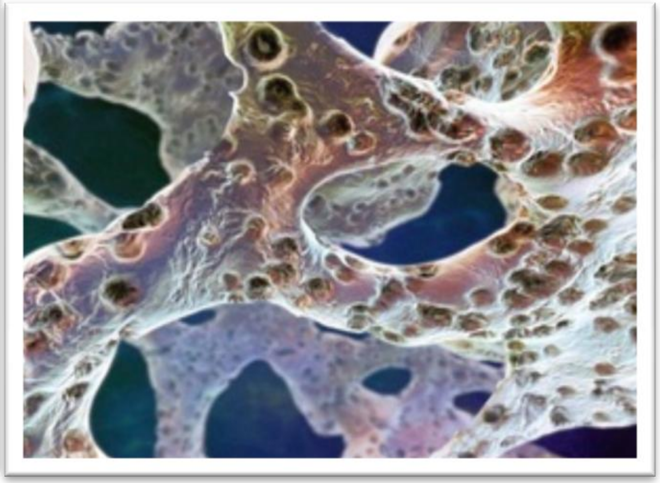
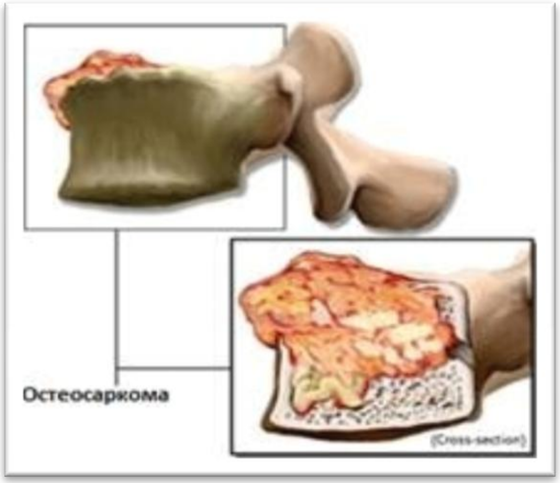
Research relevance





Biological Calcium Apatite $(Ca, Mg, Na)_{10}(PO_4, HPO_4, CO_3)_6(OH, F, Cl)_2$

Synthetic silicon-substituted hydroxylapatite $Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$

The purpose and objectives of the study

Purpose of the study:

to establish the regularities of changes in physicochemical properties, phase composition of silicon-containing hydroxylapatite in a gelatin matrix synthesized from a solution by the biomimetic method and composites based on it from the parameters of a model solution emitting human extracellular fluid (simulated body fluid, SBF).

Tasks:

1. Propose the conditions for obtaining a solid composite based on HA-gelatin, Si- HA-gelatin from a model solution SBF.

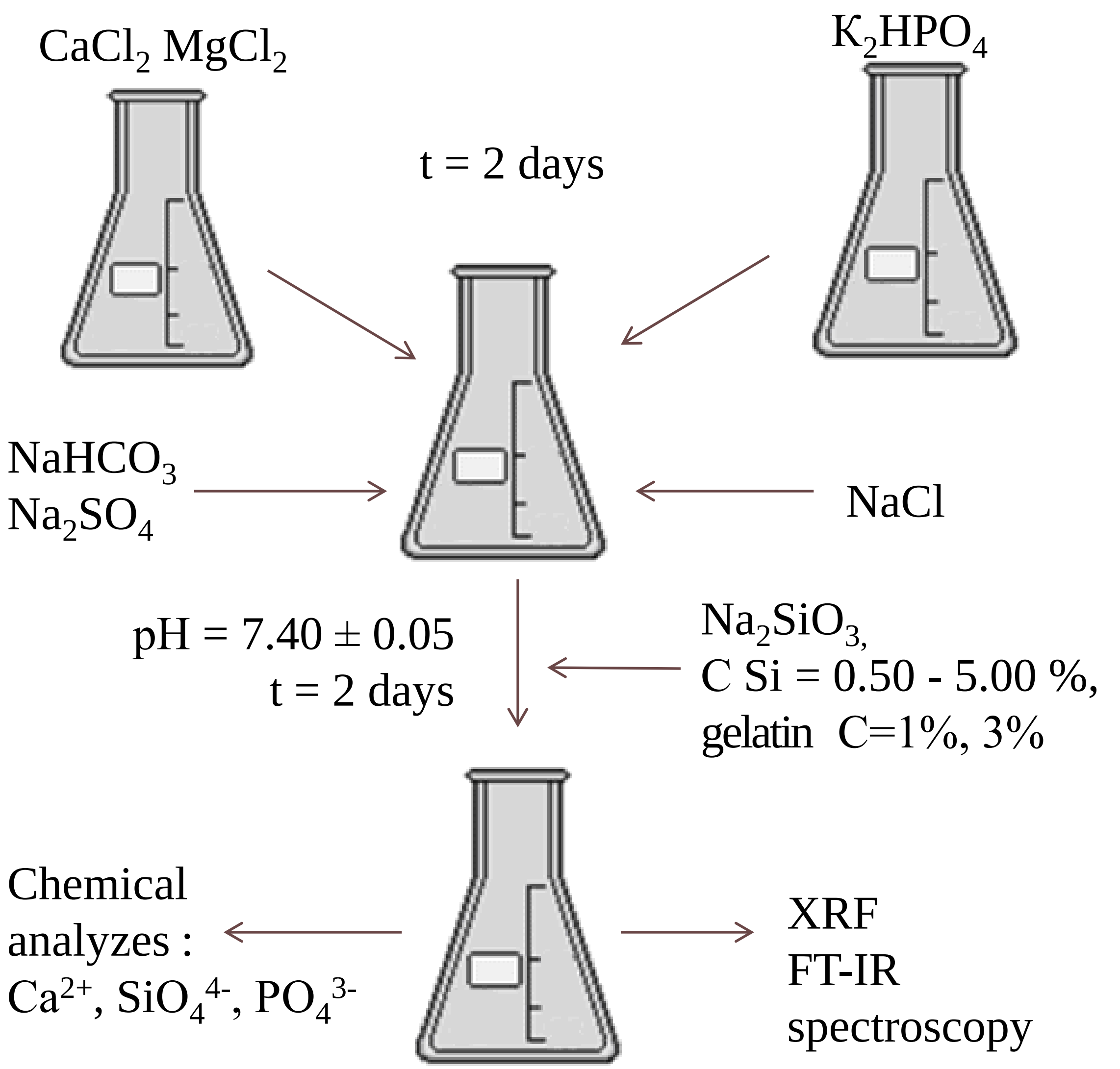
2 Investigate the thermal stability and bioactivity of the materials obtained. To analyze the processes of destruction and establish the kinetic regularities of dissolution of samples containing GAS and biocomposites based on them.

3. To study the possibility of obtaining biocomposite coatings based on on HA-gelatin, Si- HA-gelatin on VT1-0 titanium alloys. Determine the optimal conditions for the physicochemical treatment of the obtained alloys. Identify the coating with the best adhesive and bioactive properties.

Method for the synthesis of modified hydroxylapatite from a model solution of extracellular fluid

Inorganic composition of the model solution of extracellular fluid«Simulated Body Fluid»

Composition	C, mmol/L
Ca^{2+}	2.5
Na^{+}	142
K+	5
Mg^{2+}	1.5
Cl^{-}	105
HPO_4^{2-}	1
HCO_3^{2-}	27
SO_4^{2-}	0.5

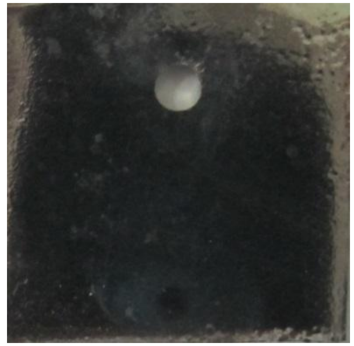


Basic methods of analysis

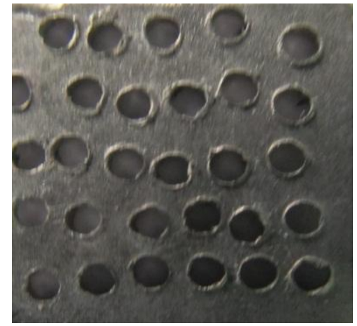
№ п/п	Method	Tasks to be solved
1	X-ray phase analysis	Qualitative and quantitative determination of the phase composition of the sample
2	FT-IR spectroscopy	Characterization of the mineral component of the sample, determination of the presence of main groups and water molecules
3	Atomic Emission Spectrometry	Determination of the Ca / P ratio in samples
4	TGA	Determination of thermal effects, weight loss during calcination up to 1000^0C
5	Spectrophotometric Analysis	Determination of the content of phosphate-ionoa in solution
6	Potentiometric Analysis	Determination of the content of calcium and hydrogen ions in solution
7	Optical / electron / force microscopy	Study of the surface and morphology of the sample

Titanium substrate processing methods

Without processing



Etched HF:HNO_3 (1:1)



Perforated

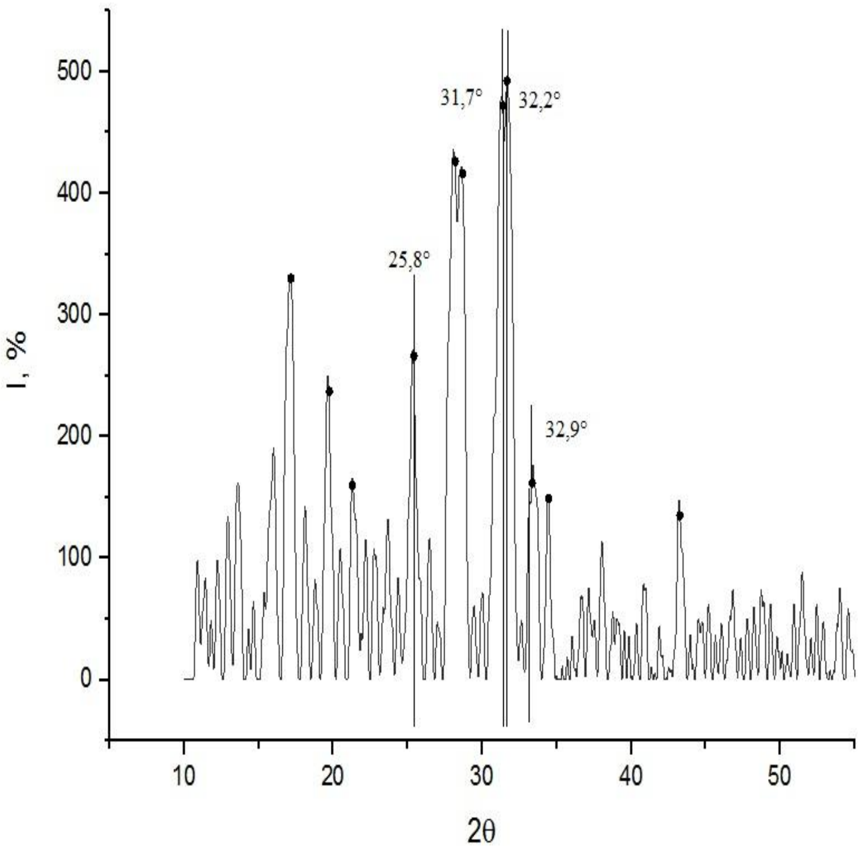
Perforated etched

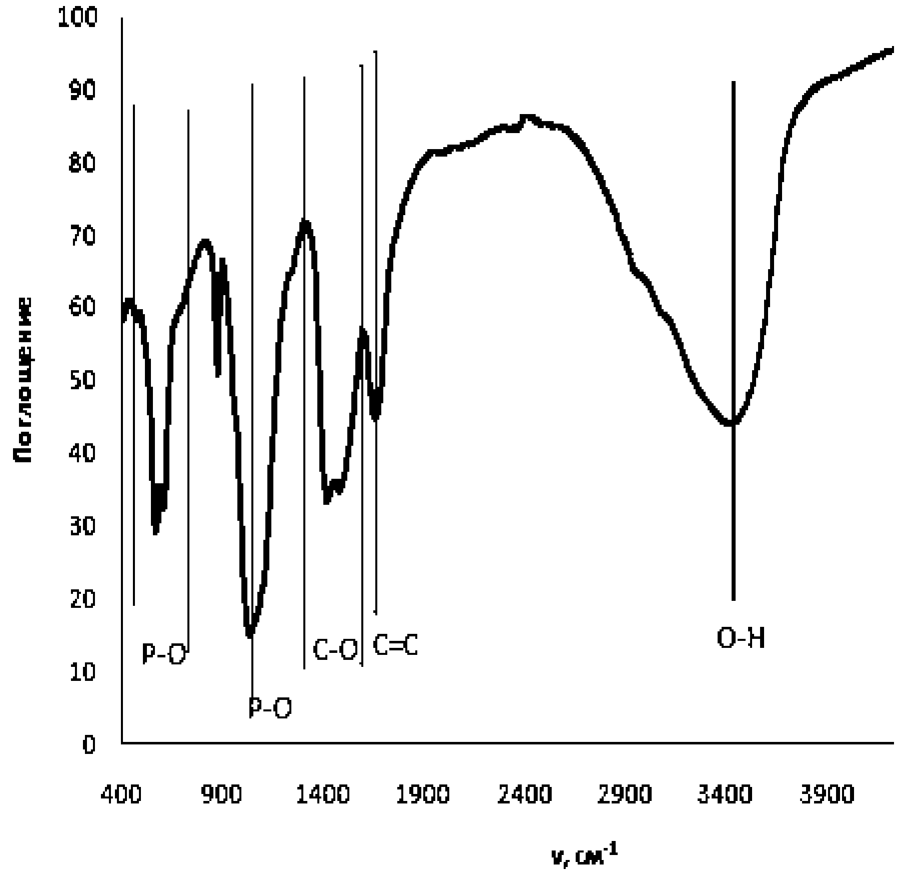
Sanded processed MIP

	Fe	C	Si	N	Ti	O	H
Ti BT1-0, %	<0,18	<0,07	<0,1	<0,04	98,61-99,7	<0,12	<0,01

Composition of titanium alloy VT 1-0

Results of XRD and IR spectroscopy of HA-gelatin



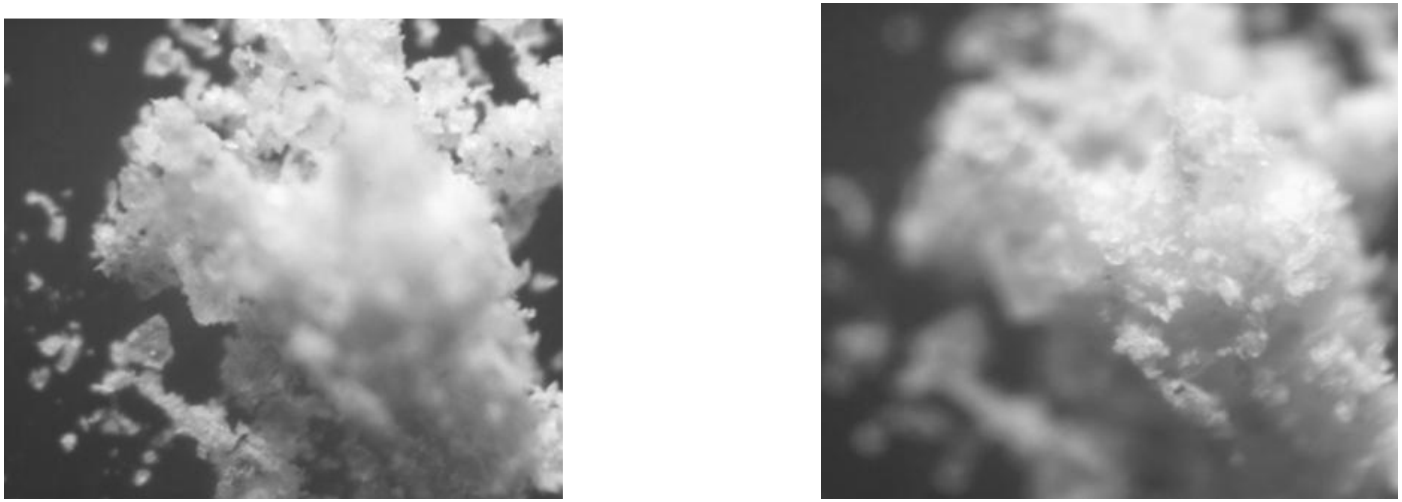


XRD a sample of hydroxylapatite synthesized in the presence of a 3% gelatin solution

IR spectrum a sample of hydroxylapatite synthesized in the presence of a 3% gelatin solution

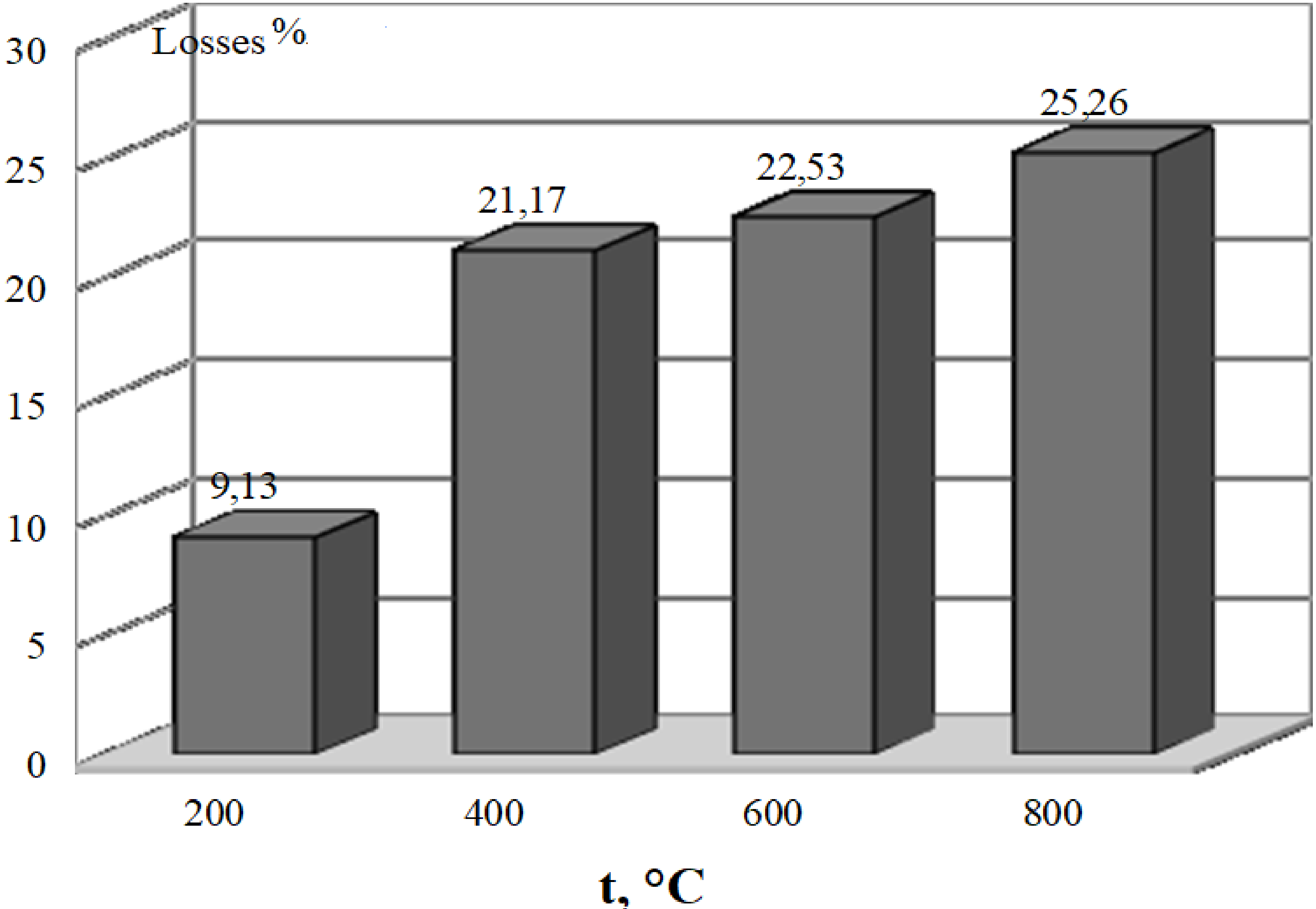
Results of crystal lattice parameters and optical microscopy of HA-gelatin

Sample	C gelatin, %	Lattice constant, Å	
		a	c
HA	-	9.414	6.865
HA-Gelatin	3	9.432	6.881

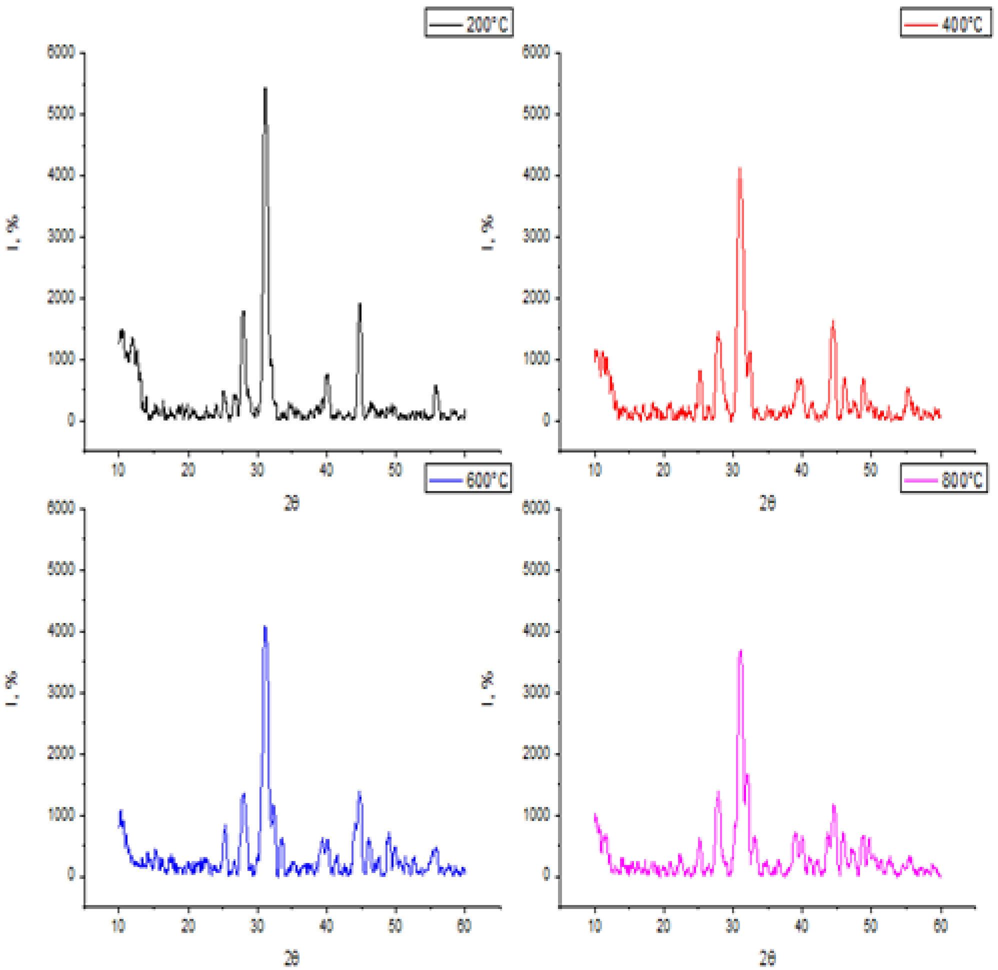


Crystallized HA powder in the presence of 3% gelatin solution (100x magnification)

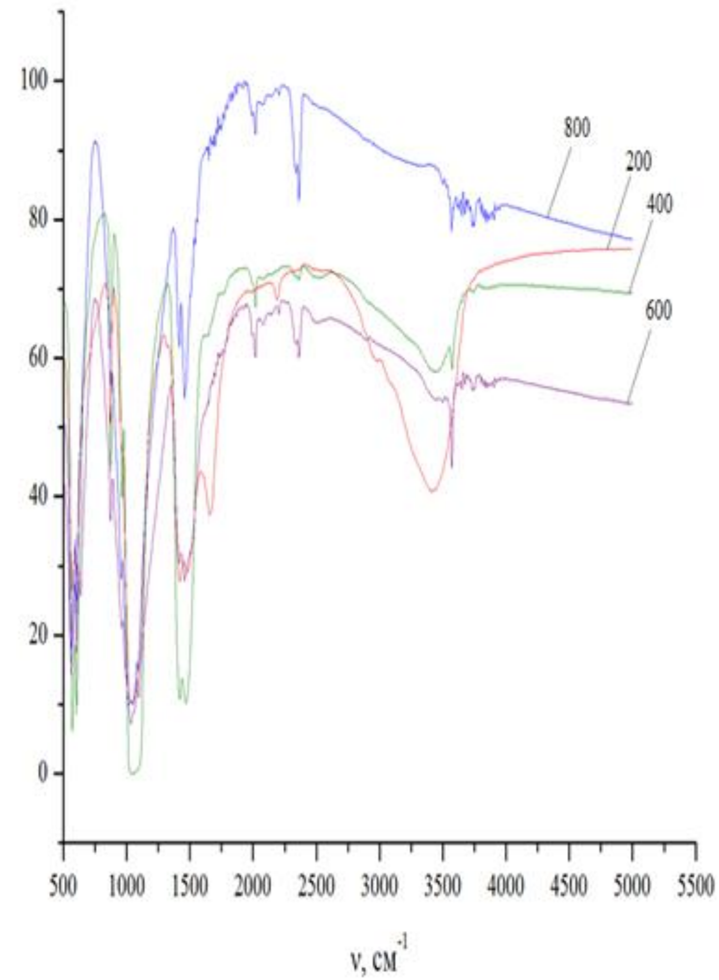
Thermal properties results HA-gelatin



Thermal properties results HA-gelatin



XRD a sample of hydroxylapatite synthesized in the presence of a 3% gelatin solution
after heat treatment

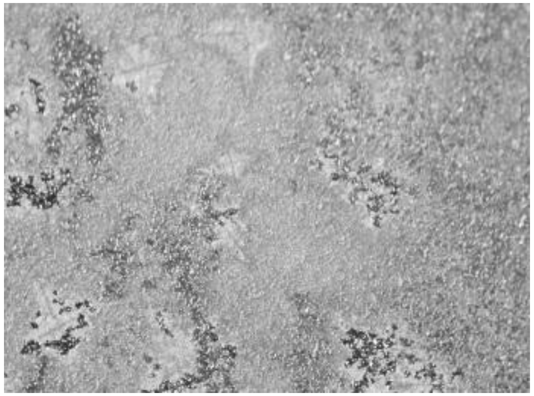


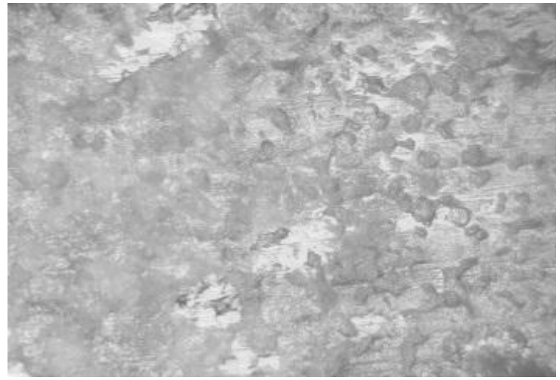
IR spectrum a sample of hydroxylapatite synthesized in the presence of a 3% gelatin solution after heat treatment

Study of the possibility of deposition of Si-HA and HA-gelatin on titanium alloy

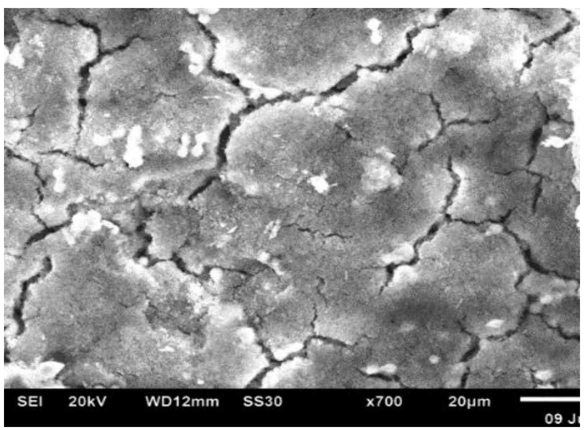
Additive	Composition	σ_{01}, MDg/m^2	cosΘ	W_a,MDg/m^2	W_k,MDg/m^2	W_a/W_k
Na_2SiO_3	1,00 %	85,12	0,73	147,26	170,24	0,87
	2,50 %	76,16	0,26	115,76	152,32	0,76
	5,00%	76,82	0,44	110,62	153,34	0,72
ТЭС	1,00 %	66,04	-1	0	132,08	0
	2,50 %	64,57	0,26	81,36	129,14	0,63
	5,00%	66,67	-0,76	16,00	133,34	0,12
Gelatin	3%	-	0,99	-	-	-

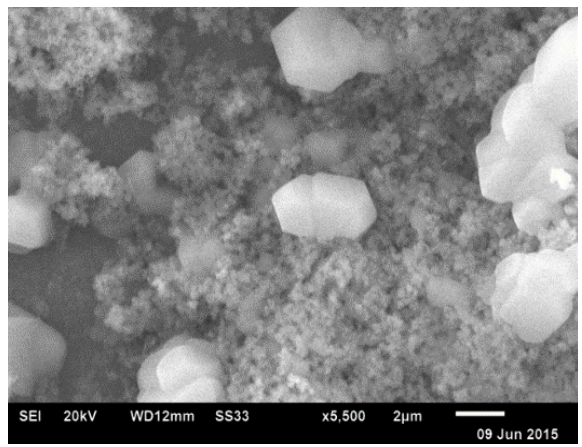
Surface morphology of Si-HA, HA-gelatin crystals on a titanium substrate

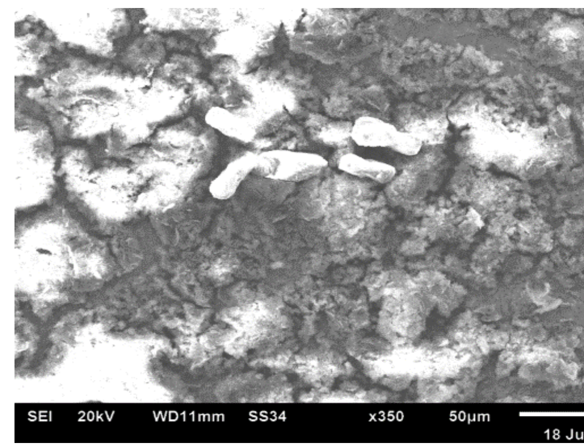




Surface morphology of hydroxyapatite crystals grown on the surface of VT1-0 titanium alloy after MIP irradiation with j = 50 A/cm^2





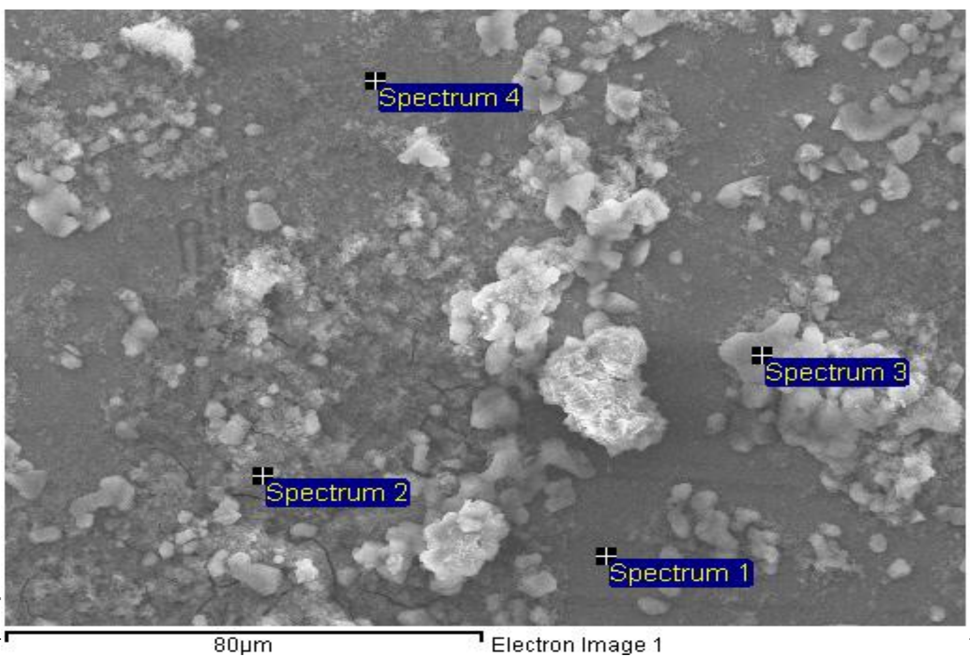


Surface morphology of HA-gelatin crystals grown on the ground surface of VT1-0 titanium alloy

Surface morphology of hydroxyapatite crystals grown on a ground surface of a titanium alloy VT1-0, after MIP irradiation

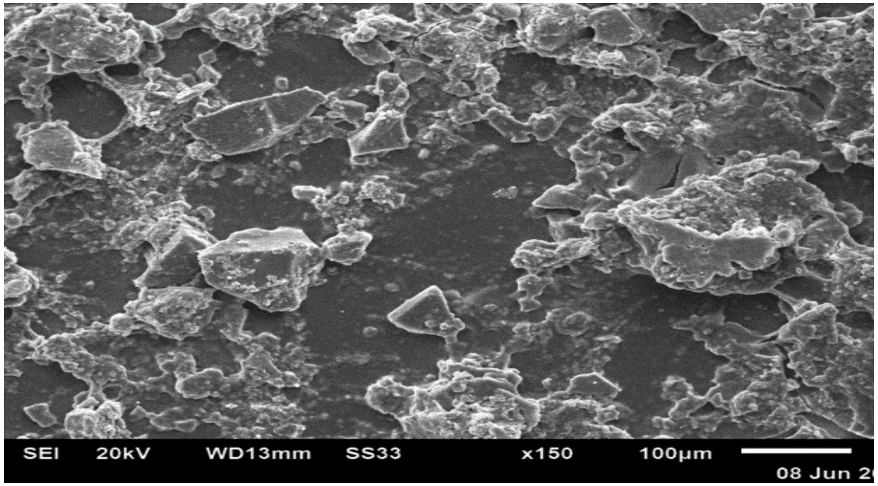
Elemental and quantitative analysis of the resulting ceramics

Points	Ca/P	C	O	Na	Mg	P	S	Cl	K	Ca	Ti
1	1.50	5.58	41.70	0.93		0.68				1.02	50.07
2	1.80	9.71	58.05	3.45	1.23	8.00	0.14	1.70	0.67	14.39	2.66
3	1.63	1.22	8.23	7.99		3.04		39.66	32.23	4.95	2.68
4	1.38	8.88	50.02	1.24	0.35	1.20				1.66	36.66

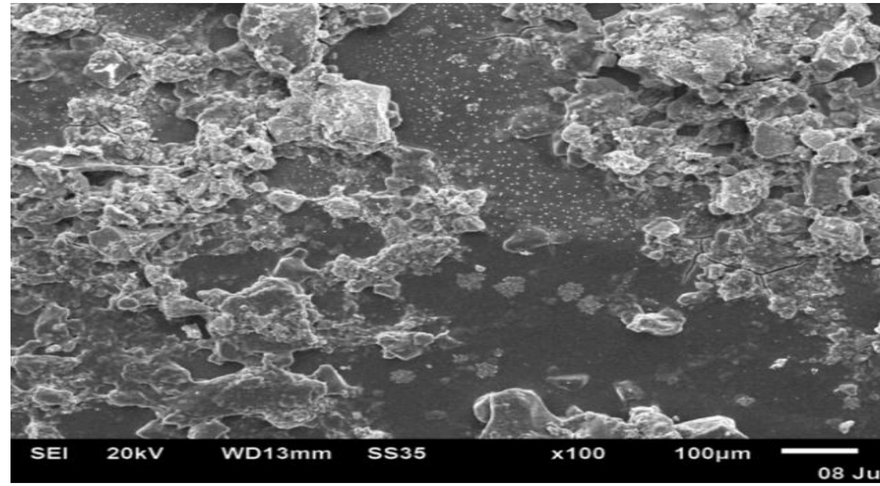


Ground surface of titanium alloy VT1-0 with grown crystals of hydroxylapatite in the presence of 3% gelatin solution

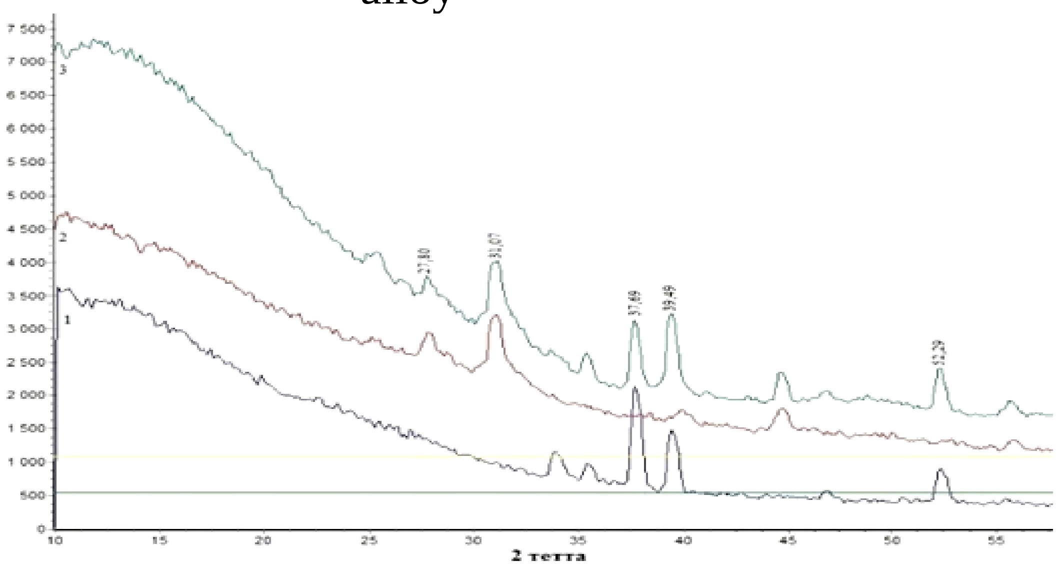
Surface morphology of Si-HA in a gelatinous matrix crystals on a titanium substrate



Surface morphology of Si-HA in a gelatinous matrix crystals deposited on VT1-0 titanium alloy

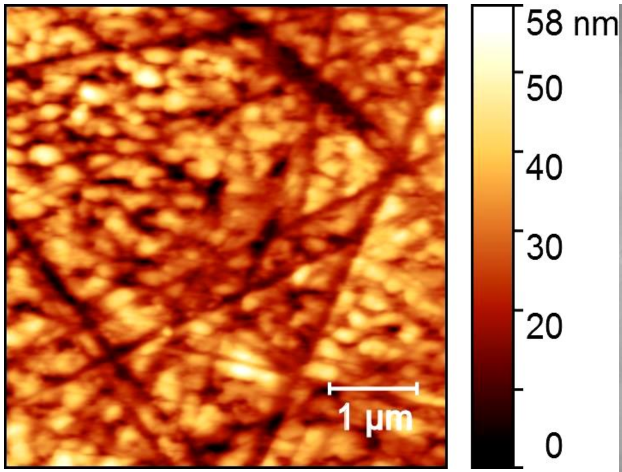


Surface morphology of HA crystals deposited on VT1-0 titanium alloy after MIP irradiation

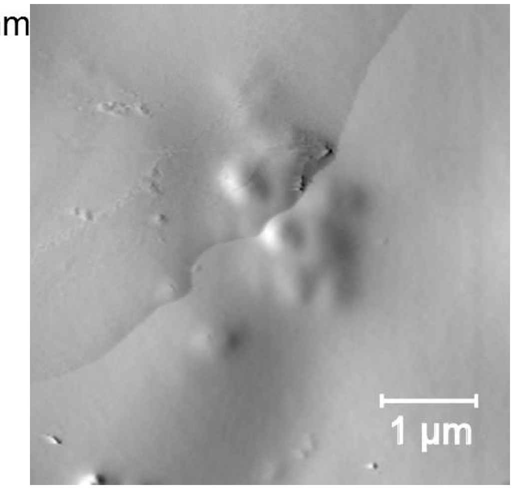


Diffraction patterns: 1 - titanium alloy VT1-0; 2 Si-HA in a gelatinous matrix C (Si) = 2.50% before irradiation; 3 Si-HA in a gelatinous matrix C (Si) = 2.50% after MIP irradiation

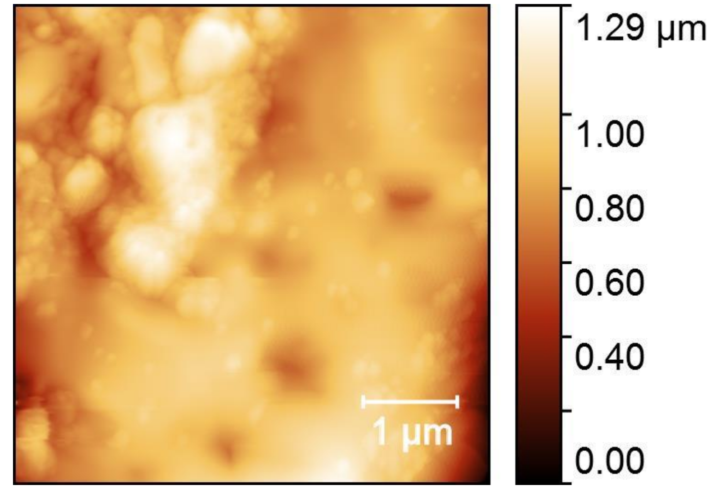
Surface morphology of Si-HA in a gelatinous matrix crystals on a titanium substrate according to AFM data



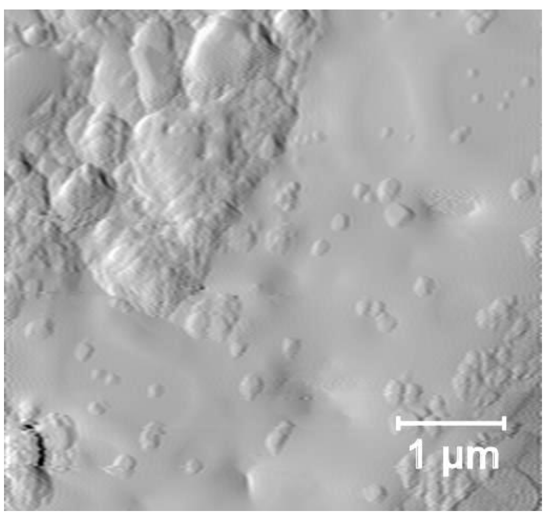
a



b



c



d

Surface morphology of hydroxylapatite crystals grown on the surface of VT1-0 titanium alloy obtained by AFM measurements: before MIP irradiation

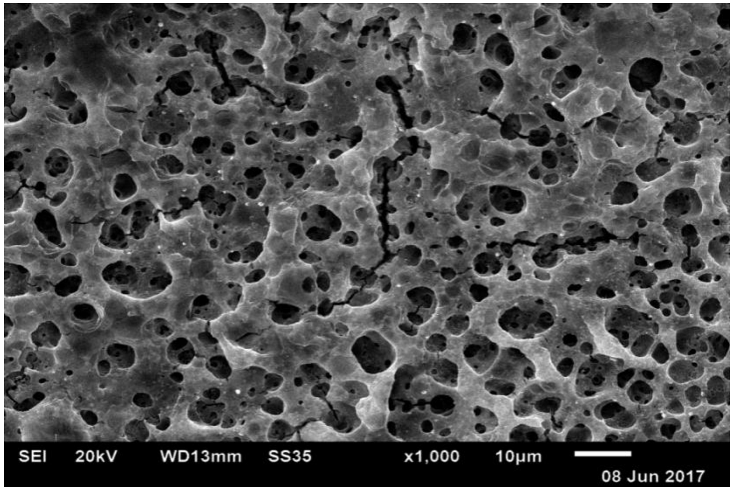
a - high-altitude contrast;

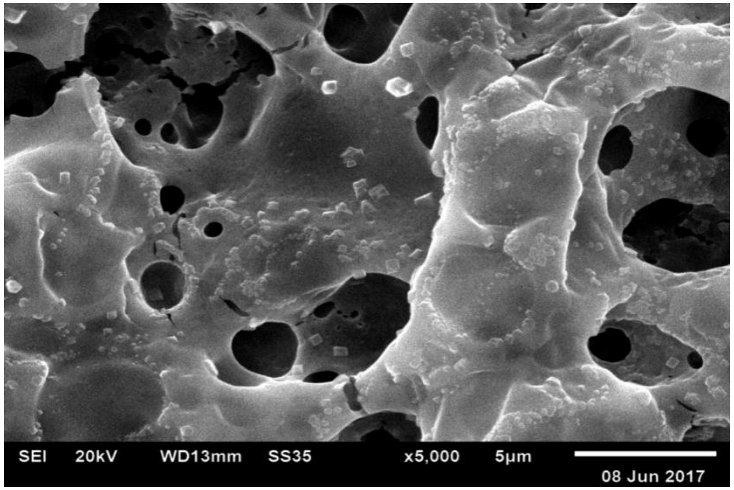
b - amplitude contrast;

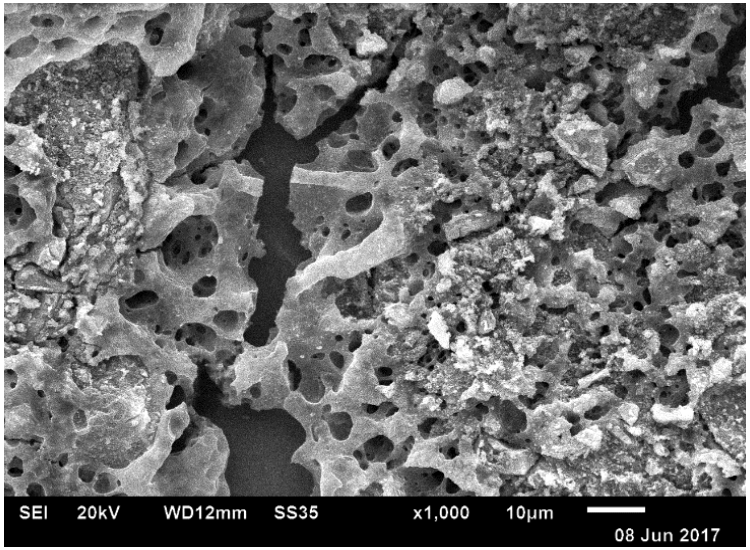
after irradiation with MIP in - high-altitude contrast;

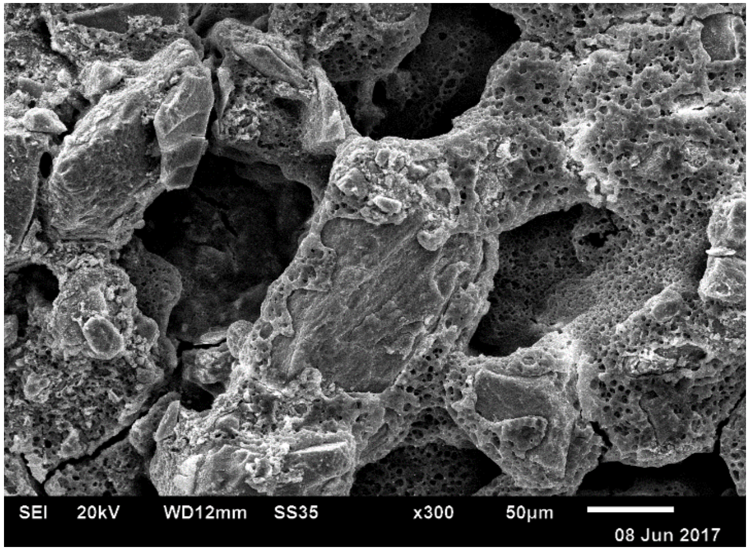
d - amplitude contrast.

Surface morphology of Si-HA in a gelatinous matrix crystals on a titanium substrate after MIP irradiation



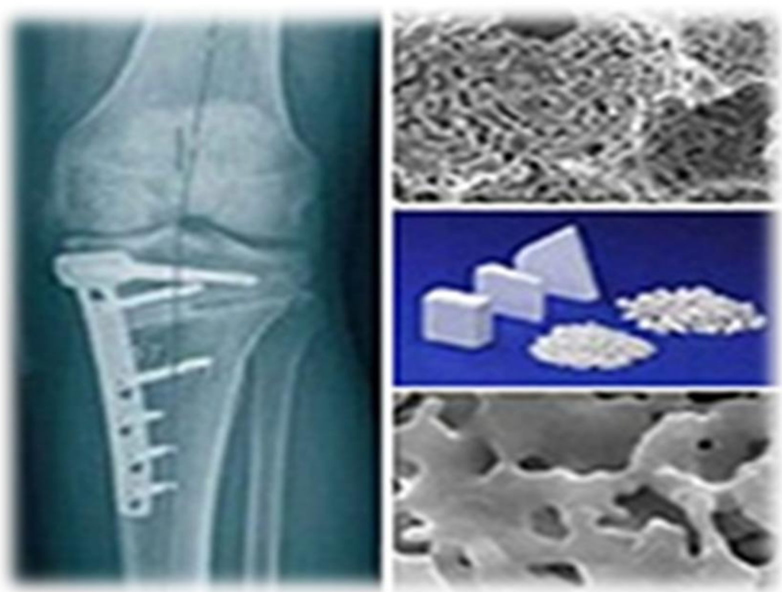


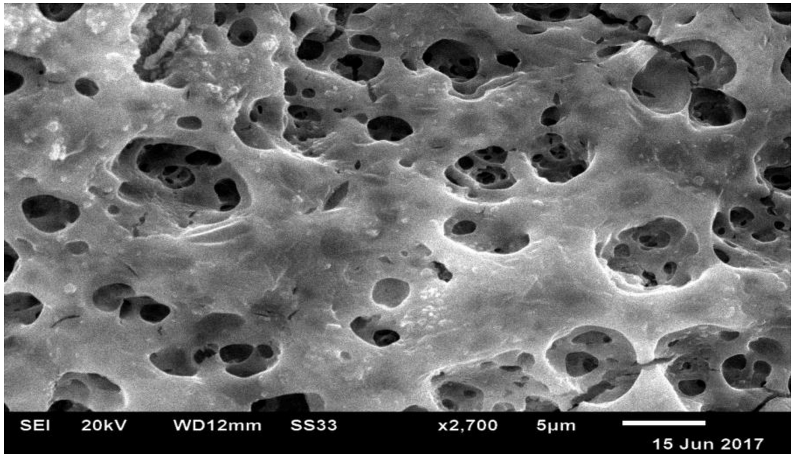




Density and porosity measurements

Sample	Density, d, g/cm^3	Porosity, P, (%)
HA	0,78	64
Si-HA in a gelatinous matrix	0,49	79
Si-HA in	0,73	71





Morphology of Si-HA in a gelatinous matrix crystals on a titanium substrate

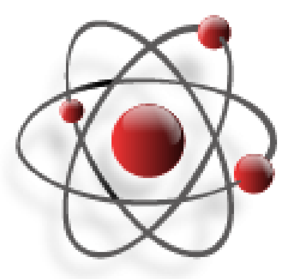
CONCLUSIONS

- The process of crystallization of calcium phosphates from a model solution of human extracellular fluid has been studied. An original method of biomimetic synthesis of HA-gelatin and Si-HA in a gelatinous matrix from a solution close in ion-electrolyte composition to human extracellular fluid has been proposed and patented. It was found that all synthesized samples are single-phase and represent hydroxylapatite. The nature of the reagent and the variation in the concentration of the modifier do not affect the phase composition of the sediments.
- It is shown that HA-gelatin samples (3 wt% gelatin) have low thermal stability and their destruction occurs at 400°C.
- In the course of studying the surface and morphological characteristics of the obtained HA-gelatin coatings on VT1-0 titanium, it was found: an increase in the concentration of silicate ions in the composition of the precipitate leads to a decrease in the wettability of the titanium sample surface and low values of the cohesion energy; The deposition of HA-gelatin and Si-HA in a gelatinous matrix on the surface of titanium substrates occurs better on etched samples.

CONCLUSIONS

- It was found that the formation of a coating of HA-gelatin and Si-HA in a gelatinous matrix on VT1-0 titanium proceeds in three stages: crystallization of crystallites by a coating of a titanium plate of a gelatin film, then the growth of crystallites in the form of dendrites, and then upward in the form of cylindrical columns with the formation of islands. MIP irradiation of the surface of the samples with the applied suspension of hydroxyapatite promotes strong fixation of the layer and the formation of crystallization centers for subsequent crystal growth.
- The materials synthesized as a result of this study can be recommended for use in orthopedics, dentistry, reconstructive surgery, traumatology, and the development of new forms of medical products that promote targeted drug delivery.

Спасибо за внимание



Методика расчета энергии адгезии и когезии*

,

$W_a = \sigma_{01}(1+\cos\Theta)$

где W_a – энергия адгезии, σ_{01} – поверхностное натяжение на границе газ - жидкость

$\cos\Theta$ - косинус краевого угла смачивания

$$\frac{W_a}{\sigma_{01}} = 1+\cos\theta$$

$$\frac{W_a}{2\sigma_{01}} = \frac{1+\cos\theta}{2}$$

так как $W_k = 2\sigma_{01}$ то

$$\frac{W_a}{W_k} = \frac{1+\cos\theta}{2}$$

Известно, что если это соотношение близко к единице, то наблюдается хорошее смачивание и т.д.

$$\frac{W_a}{W_к} = 1 - \textit{хорошее смачивание},$$

$$\frac{W_a}{W_к} = 0{,}5 - \textit{переход}\cdot\textit{к}\cdot\textit{несмачиванию},$$

$$W_a = 0 - \textit{полное}\cdot\textit{несмачивание}.$$