The Study of the Influence of Static Magnetic Field on Brushite Crystallization in the Presence of Magnesium

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The paper describes the influence of the imposition of static magnetic field on brushite crystallization. Two different configurations of the magnetic field were used. The flasks with the precipitates were placed near the different poles. It was shown that changing the magnetic field configuration and positioning the samples in proximity to north or south poles can greatly affect their crystallinity and texture with most of them having the preferred orientation along the b-axis according to the X-Ray diffraction data. The imposition of the magnetic field also influences the microstrain ratio decreasing it significantly. It was also verified [1] that the Mg substrate availability decreases the crystallinity of DCPD. The micrographs of the nanoparticles with the different magnifications were obtained by the transmission electron microscopy (TEM). The comparative analysis of the electron microscopy data correlates with the XRD data.

Keywords: Magnetic Field, Brushite, XRD, TEM, Preferred Orientation, Magnesium.

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1. INTRODUCTION

Calcium phosphate cements based on brushite (dicalcium phosphate dehydrate, DCPD, Ca-HPO$_4$·2H$_2$O) are widely used due to their high resorbability in vivo [2]. DCPD is relatively soluble in fluids affined to the physiological ones which lead to the increase in concentration of Ca^{2+} and P$^-$ ions in the bone-implant interface. Brushite can transform into hydroxyapatite (HA) [3] in aqueous solutions at $36 - 37°C$. DCPD has the monoclinic crystal lattice (Fig. 1) [4] (space group Ia) with unit cell parameters $a = 5,812 \pm 0,002$ Å, $b = 15,18 \pm 0,003$ Å, $c = 6,239 \pm 0,002$ Å and $\beta = 116,25 \pm 2°$ [5].
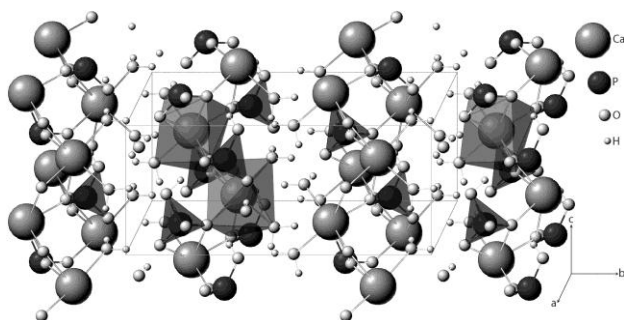

Fig. 1 – Brushite crystal lattice

Solubility and ability of brushite transformation in vivo grants certain preferences in its use as a coating for metallic implants. In addition such coatings are cheap especially when obtained on conductive porous materials with electrolysis.

Calcium-phosphate crystallization is affected considerably by different physical conditions, e.g. temperature, pH, ionic strength, presence of different additions and imposition of magnetic field.

Magnesium substrate influences DCPD and HA crystallization in the following way: Mg^{2+} ions which are formed after hydrolysis of the main corrosion product Mg(OH)$_2$ [6] decrease crystallinity of calcium-phosphates. The DCPD, metastable at room temperature, can be stabilized by the presence of the Mg substrate. According to recent studies [7] magnesium ions stabilize the brushite lattice even at pH = 7–7,5.

2. MATERIALS AND METHODS

2.1 Materials

The initial solution for calcium-phosphate precipitation contained 10 mmol·dm^{-3} CaCl$_2$ and 6 mmol·dm^{-3} Na$_2$HPO$_4$. pH of the initial solution was increased to 6,65 by adding NaOH. At pH = 6,65 the phase composition was presented by DCPD. The experiments were carried out at 25°C with and without the imposition of 0,3 T static magnetic field.

Calcium-phosphate materials were crystallized in the presence of $10 \times 10 \times 2$ mm magnesium substrates. The magnesium ion release into the solution was calculated from the mass loss of magnesium substrates and approximately equals 0.01 g/l after 2 days of precipitation.

Static magnetic field was imposed by a set of rectangular shaped $50 \times 20 \times 15$ mm Sm/Co magnets placed on a nonmagnetic base. Glasses with precursor solutions containing CaCl$_2$ and Na$_2$HPO$_4$ with Ca/P = 1,67 were placed on both sides of magnets in proximity to south and north poles (Fig. 2) with each glass containing a single Mg substrate.

The magnetic intensity of 0,3 T was measured in proximity to south and north poles using a Gauss-/Teslameter F 54 (Magnet-physik Dr. Steingroever GMBH).

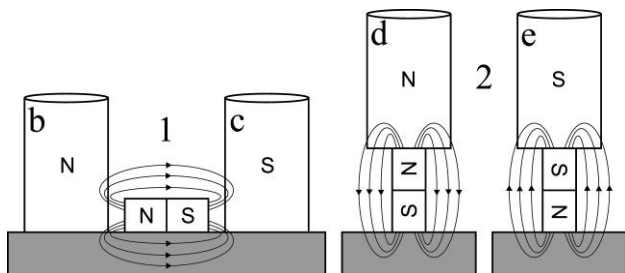* vkuznetsov.ua@gmail.com

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Fig. 2 – Experimental setup showing the two magnetic field configurations and samples names

2.2 Methods

The crystallinity and structure of the synthesized samples were examined using an X-ray diffractometer DRON-4-07 (Bourevestnik, Inc., Saint-Petersburg, Russian Federation) connected to a computer-aided system for the experiment control and data processing. The Ni-filtered CuKα radiation (wavelength 0,154 nm) with a conventional Bragg-Brentano θ-2θ geometry was used. The current and the voltage of the X-ray tube were 20 mA and 40 kV respectively. The samples were measured in the continuous mode at a rate of 1 °/min with 2θ-angles ranging from 15° to 55°. All experimental data was processed by means of the program package DIFWIN-1 (Etalon PTC, Ltd., Moscow, Russian Federation). Identification of crystal phases was done using a JCPDS card catalog (Joint Committee on Powder Diffraction Standards).

The crystallite sizes L were calculated using the Scherrer equation and by the Williamson-Hall method considering the influence of small sizes of coherent scattering regions and deviations of interplanar spaces between a sample and a standard in which microstrains ε are absent using the Cauchy approximation function for each contribution characterization on the peak broadening.

The texture estimated values Φ were calculated using the Harris method [8]:

$$\Phi = n \frac{I_i}{I_i^{st}} \left(\sum_{i=1}^{n} \frac{I_i}{I_i^{st}} \right)^{-1}, \qquad (2.1)$$

where n – number of peaks used in estimation, I_i – the sample intensity of peak i, I_i^{st} – the standard intensity of peak i. The data from JCPDS 72-713 card was used as a standard for the sample precipitated without the imposition of static magnetic field. This sample was used as a standard for the samples precipitated with the imposition of static magnetic field.

Electron microscopic studies were conducted after the ultrasonic dispersion of the samples using the transmission electronic microscope PEM-125K (SELMI, PTC, Sumy, Ukraine) with the 90 kV accelerating voltage and the 100 μA beam current. The samples were treated with the ultrasound using UZDN-A (Selmi, PTC, Sumy, Ukraine). The ultrasonic radiator was put into the flask with distilled water and powder samples for 5 minutes. The power density was about 15-20 W/cm² with the radiator operating frequency of 22 kHz. Next, the few drops of derived suspension were applied to the pointed upward ultrasonic radiator and

were pulverized for 2-3 seconds varying the unit power. The pulverized spray was collected by the $10 - 20$ nm carbon film put on the copper net.

3. RESULTS AND DISCUSSION

The analysis of the precipitate obtained from the solution with Ca/P = 1,67 with and without the imposition of magnetic field in the presence of a Mg substrate after two days of precipitation shows the occurrence of a single phase – brushite (JCPDS 72-713).

The crystallinity of b- and c- samples of the first magnetic field configuration (1C) remains comparable to the sample, precipitated without the imposition of magnetic field (a-sample), with the crystallinity of the b-sample slightly better than the c- one (Fig. 3).

In case of the second magnetic field configuration (2C) the crystallinity perceptibly increases compared to the a-sample. The d-sample has much higher intensities of (0 4 0) and (0 8 0) peaks which means that it is oriented along the b-axis.
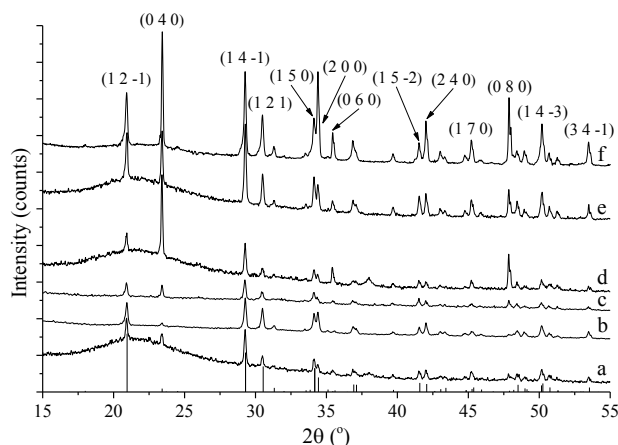

Fig. 3 – XRD spectra of samples with and without the imposition of magnetic field in the presence of Mg and without it (f)

The mean crystallite sizes (Table 1) of the 2C in most cases are higher than the 1C ones. The crystallite sizes of the a-sample and 2C samples differ insignificantly with the visible distinction in their crystallinity which can be explained by the presence of lattice strains in the a-sample.

Due to the availability of the peaks corresponding to the planes laying in the same crystallographic direction the Williamson-Hall method was used to separate contributions of different factors in the peak broadening. The derived results show that the a-sample has a much higher value of microstrains than the other samples thus proving the hypothesis noted above.

The preferred orientation varies depending on the magnetic field configuration and the proximity to the different poles. Most of the samples (c, d and e) have the highest texture values in [0 k 0] direction with only the b-sample having them in (1 2 1) and (2 0 0) planes. It should be mentioned that the initial a-sample has the highest texture in [0 k 0] direction however the other samples texture values are 1,6-4,3 times higher.

The effect of the magnesium substrate presence in the initial solution for calcium-phosphate precipitation on brushite crystallization was also studied. It was veri-

fied [1] that the Mg substrate availability decreases the crystallinity of DCPD (Fig. 3a).

Table 1 – The mean crystallite sizes, texture and microstrain values of the precipitated samples in the presence of magnesium

Samples		a	b	c	d	e
(121)	L, nm	70	52	51	64,2	63,4
	Φ	0,209	0,97	0,871	0,408	0,793
(040)	L, nm	55,6	65,4	81,5	96,6	78
	Φ	1,892	0,26	1,709	4,285	1,697
(121)	L, nm	58,8	53,5	53,7	55	73,7
	Φ	0,266	1,642	1,05	0,354	0,989
(150)	L, nm	66	54,8	50	61,5	67,7
	Φ	0,342	1,13	1,003	0,42	0,847
(200)	L, nm	71,3	60,6	112,6	84,2	77,2
	Φ	0,342	2,179	0,955	0,467	1,146
(080)	L, nm	112	83	84,6	113,5	97,6
	Φ	3,335	0,345	1,752	3,218	1,64
W-H	L, nm	37	54	78,6	84	64,8
	$\varepsilon \cdot 10^{-3}$	1,47	0,37	0,17	0,043	0,24

The micrographs of the nanoparticles with the different magnifications were obtained by the TEM (Fig. 4). The particle sizes are: a-sample $-50-60$ nm, b-sample $-40-80$ nm, c-sample $-30-60$ nm. The comparative analysis of the electron microscopy data correlates with the XRD data. The higher sizes of the particles in case of the b-sample can be explained due to the differences between the crystallite and particle sizes thus considering that in this case the particles consist of two or more crystallites.
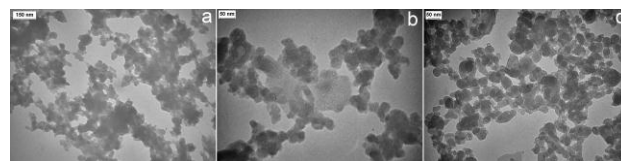

Fig. 4 – Micrographs of the nanoparticles with the different magnifications of a-, b- and c- samples

4. CONCLUSIONS

The imposition of magnetic field influences greatly the crystal structure of DPCD. The different configurations of magnetic fields and proximity to different poles lead to the changes in crystallite and particle sizes, preferred orientations and microstrain values which provide the ability to control the properties and, thus, the biomedical applications of this material. It should be mentioned that the precipitation under the imposition of magnetic field significantly decreases the crystal structure microstrains.

It was also verified that the presence of the Mg substrate in a calcium-phosphate precipitation solution decreases the crystallinity of DCPD.

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