Study on the processes of nitrogen adsorption and capillary condensation in the powders of calcium hydroxyapatite

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Abstract. This work is devoted to the study of mesoporous structure parameters of calcium hydroxyapatite powders on the basis of data obtained by nitrogen thermal desorption method. The isotherms of nitrogen desorption/adsorption on the samples of hydroxyapatite and the changes in their porous structure parameters depending on the temperature of the heat treatment are discussed.

1. Introduction

Calcium hydroxyapatite (HAP) is widely used in such areas of medicine as dentistry and bone engineering, as bioceramic and defect-substituting material. The study of the processes of nitrogen adsorption and capillary condensation allows one to investigate the parameters of the porous structure of HAP, which is an important indicator for its use in medicine. Natural calcium hydroxyapatite is the basis of human bone tissue and is about 50% of the total bone mass, as well as almost 96% of human enamel. Synthetic HAP is biocompatible with the human body, this fact gives an opportunity to use it as a material for bioceramics, replacement of defects and regeneration of bone tissue [1], as well as for targeted drug delivery [2].

The surface properties of HAP, which greatly depend on the parameters of the porous structure such as the specific surface area and pore size distribution, are very important for determining its effectiveness and conditions for using in medicine. HAP is a mesoporous material (its pore sizes lie in the range from 2 to 50 nm), in which there is a capillary condensation process: at a relative pressure within 0.4 – 1, the volume of mesopores is filled with the liquid phase of the gas-adsorbate [3]. Capillary condensation is an irreversible process, since the sorption values do not coincide when the pressure of the sorbent increases and decreases. The aim of this work is to study the changes in the parameters of the porous structure of hydroxyapatites, such as specific surface area calculated with the use of BET method and pore size distribution, depending on the conditions of the heat treatment of the HAP powders.

2. Experiment

The HAP samples were obtained by the chemical bath deposition method [4]: the solutions of calcium nitrate (Ca(NO$_3$)$_2$·4H$_2$O) and diammonium phosphate ((NH$_4$)$_2$HPO$_4$) were used as the precursors. The solutions with various concentration were taken: (NH$_4$)$_2$HPO$_4$ with a concentration of 0.25 M and Ca(NO$_3$)$_2$·4H$_2$O with a concentration of 0.15 M. The solutions were obtained using a magnetic stirrer at a speed of 300 rpm, temperature of 25°C during f 5 minutes. The ((NH$_4$)$_2$HPO$_4$) solution (50 ml)
was gradually added to the (Ca(NO$_3$)$_2$·4H$_2$O) solution of the same volume. The reaction took place in a thermostat at the temperature of 60°C. To maintain the pH value of 9, the 25 % ammonia solution was used. The resulting precipitate was filtered for 30 minutes using a filter paper with a pore size of 5 μm. This way, a set of the samples subjected then to heat treatment was obtained.

The study of adsorption and capillary condensation processes was carried out using the MS Sorbi device («META», Novosibirsk, Russia) intended to study the specific surface area and the porous structure parameters of dispersed and porous materials [5, 6]. The thermal desorption method was used to measure the amount of adsorbed gas. The analysis of adsorption isotherms was carried out using a special program developed at Saint Petersburg Electrotechnical University «LETI» [7, 8].

3. Results and discussion
In the course of the work, five types of HAP powder samples were obtained and investigated: one type was without heat treatment, the other types were annealed at the temperatures of 150 °C, 300 °C, 600 °C, 900 °C. The heat treatment time was 60 minutes in each case. The full adsorption/desorption isotherms for the samples are presented in Figures 1 – 5 (figures 1 -5 show the adsorption lines in blue and the desorption lines in red).
Figure 5. Full adsorption/desorption isotherm for the HAP powder after heat treatment at the temperature of 900 °C

With the use of the obtained data on adsorption isotherms (Figure 1 - 5), the histograms of the pore distribution over sizes (Figure 6) were obtained.

Figure 6. The histograms of the pore distribution over sizes depending on the temperature of heat treatment

From the Figure 6 it can be seen that there are no pore systems with an average radius of 4.2 and 12 nm in the samples with a heat treatment temperature of 900 °C. This fact is explained by the coalescence of the pores during heat treatment.

Table 1 shows the obtained values of the specific surface area (SSA) depending on the heat treatment conditions.

Table 1. The data on the specific surface area for HAP powders calculated by the BET method

| T, °C  | SSA, m²/g |
|--------|-----------|
| Without treatment | 54        |
| 150    | 80        |
| 300    | 89        |
| 600    | 49        |
| 900    | 7         |
The relatively small specific surface area of the samples without heat treatment is caused by the presence of humidity, which was removed in all other samples during the heat treatment. The decrease of the specific surface area at 900 °C is due to increasing of the pore sizes. This fact correlates with the histogram of the pore size distribution and with the disappearance of the pore system with an average radius of 4.2 and 12 nm during sintering.

4. Conclusions
In the work hydroxyapatite calcium powders were obtained via chemical bath deposition method, the powders were heat treated at different annealing temperatures. The temperature of heat treatment significantly affects the specific surface area, the dimensions of the mesopores and their quantity in the material under study. It has been established that after an increase in heat treatment temperature, a significant amount of pores increases in size, which leads to a decrease in the specific surface area.

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