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Mass Spectrometric Study of Evaporation of Hydroxyapatite at Temperatures up to 2200 K

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Abstract—The composition of the gas phase was identified for the first time up to a temperature of 2200 K by the Knudsen effusion mass spectrometric method, and the partial pressures of the vapor species during the evaporation of hydroxyapatite were determined. $Ca_{10}(PO_4)_6(OH)_2$ was evaporated from a Knudsen effusion cell made of tungsten. In the temperature range 1200–1300 K, $Ca_{10}(PO_4)_6(OH)_2$ undergoes dehydration, forming $Ca_3P_2O_8$, which evaporates in the form of PO, atomic calcium, and oxygen when the temperature further increases to 1750–2200 K.

Currently, composite biomaterials based on calcium phosphates are very promising for implantation medicine due to their biocompatibility, nonrejection by the body, bioactivity, and successful integration into living bone tissue [1−7]. That is why the development of methods for the synthesis of biomaterials based on calcium phosphates is one of the most important trends in modern materials science. Basic calcium monophosphate $Ca_{10}(PO_4)_6(OH)_2$, known in the literature as hydroxyapatite, is the main inorganic component of the bone and dental tissues of a living organism.

Among the variety of currently used approaches to the synthesis of hydroxyapatite, precipitation from aqueous and nonaqueous solutions is the best known and thoroughly developed method [8].

Nonaqueous media are generally used in the synthesis of $Ca_{10}(PO_4)_6(OH)_2$ to prevent possible hydrolysis of the desired product and introduce in it carbon dioxide dissolved in water in the form of carbonate ions. Precipitation from aqueous solutions for this purpose is less common. Hydrothermal synthesis is also successfully used to synthesize hydroxyapatite.

Solid-phase approaches are also used in addition to solution synthesis methods. The synthesis is performed at high temperatures, which can lead to dehydration of $Ca_{10}(PO_4)_6(OH)_2$, forming calcium phosphates.

The ceramics obtained from hydroxyapatite has low mechanical properties [9, 10]. This significantly limits its use to fields where loading is excluded [11]. It was established, for example, that annealing of hydroxyapatite to a temperature of 1273 K leads to compaction of the material, accompanied by an increase in the microhardness of ceramics based on it from 52 to 183 HV units [12]. A study of the morphological changes in hydroxyapatite nanopowders during thermal annealing showed [13] that the crystal structure of hydroxyapatite nanopowder is maintained in the temperature range 773−1073 K, and an increase in the annealing time leads to a decrease in the powder fineness, accompanied by crystallographic faceting of nanoparticles. A detailed study of the effect of heat treatment on the sintering and strength of ceramics prepared from hydroxyapatite nanopowders showed that the dependence of the strength of ceramics on the treatment temperature has a maximum at 973 K [10]. The appearance of this maximum, according to [10], is due to the competing influence of residual porosity and grain size on the strength.

To increase the strength of hydroxyapatite, it is also reinforced with dispersed particles of inorganic compounds [14], which necessitates further studies to understand the physicochemical processes occurring in hydroxyapatite at high temperatures, including evaporation of its components.

As a result of the thermal analysis of hydroxyapatite performed in [12], previously obtained data were confirmed [15], indicating that starting from 1073 K, partial decomposition of the sample is observed with formation of β-tricalcium phosphate, and at 1273 K further decomposition to α-tricalcium phosphate occurs and is completed at 1393 K according to [15]. It should
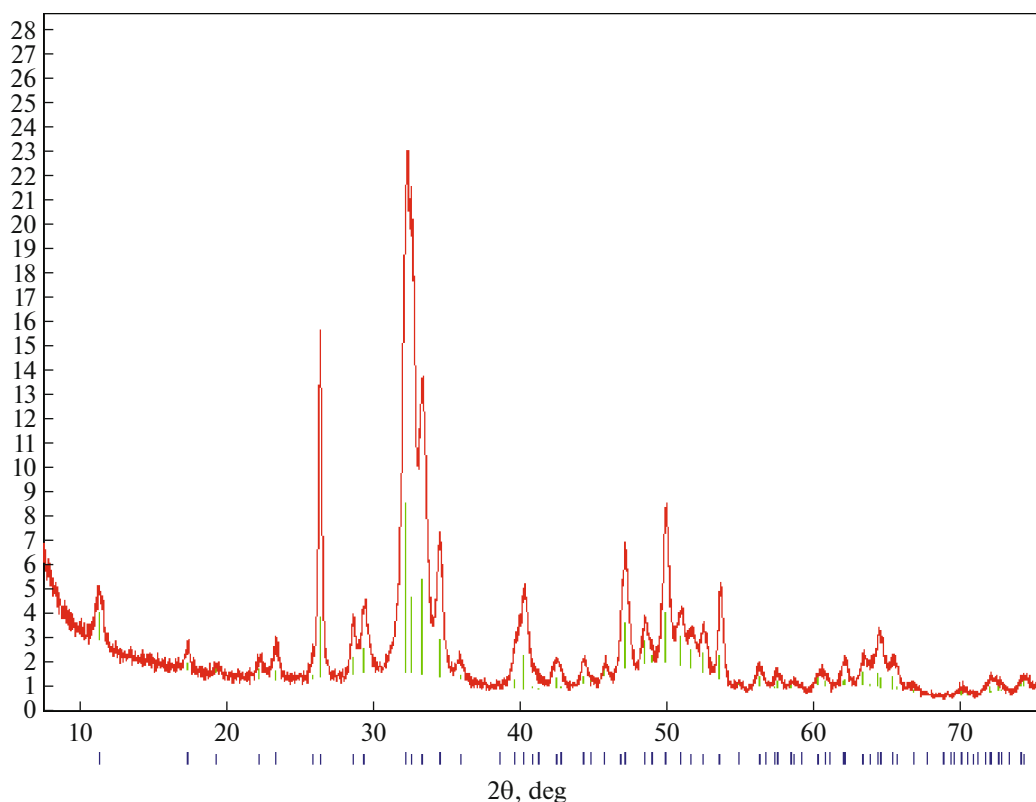
Fig. 1. X-ray diffraction pattern of the synthesized $Ca_{10}(PO_4)_6(OH)_2$.

be emphasized that these transformations were also observed in [12], and were accompanied by the endo effects on the DTA curve.

In view of the growing interest in the improvement of the mechanical properties of hydroxyapatite using high-temperature heat treatment processes, the goal of this study for the first time was a high-temperature mass spectrometric study of hydroxyapatite up to 2200 K, which made it possible to obtain unambiguous results on the change in the vapor composition and partial pressures of the vapor species over hydroxyapatite with increasing temperature.

EXPERIMENTAL

Hydroxyapatite was synthesized by coprecipitation of calcium nitrate and ammonium dihydrogen phosphate from aqueous solutions. The starting substances were dissolved in water while stirring with a magnetic stirrer. At a solution temperature of 323 K, a concentrated ammonia solution was added dropwise to the solution. Precipitation occurred for 2 h. During this time, pH was maintained at a constant value of 10 while adding the ammonia solution. After pH ceased to change, the solution was kept with vigorous stirring at the same temperature for another 2 h. After the synthesis was completed, the precipitate was filtered off

and dried, first in a stream of air, and then in a drying oven at a temperature not exceeding 323 K.

The resulting hydroxyapatite sample was identified by X-ray diffraction analysis using a Rigaku MiniFlex II X-ray diffractometer (CuK_α radiation). A comparison of the obtained diffraction pattern of the sample with the available data for hydroxyapatite showed the presence of only the reflections of the hydroxyapatite structure (01-072-1243 ICDD (PDF-2/Release 2011 RDB)) and the absence of reflections of any other phases. Figure 1 shows the obtained diffraction pattern; the reflections of the hydroxyapatite phase were assigned as shown by the bar diagram.

The transition of hydroxyapatite into the gas phase was studied by high-temperature mass spectrometry on an MS-1301 mass spectrometer, designed to study physicochemical processes occurring during the evaporation of low volatile substances. Ionization of the vapor species was performed with slow electrons with an energy of 30 eV. The sample was evaporated from a single Knudsen effusion cell made of tungsten. The cell with the sample was heated by electron bombardment; the temperature was measured with an EOP-66 optical pyrometer with an accuracy of ± 10 K. The measurement technique is described in detail in [16, 17].

In the mass spectrum of vapor over hydroxyapatite in the temperature range of 1200−1300 K, a signal of

the H_2O^+ ion was observed, which was partially obscured by the shutter of the mass spectrometer, separating the useful signal from the background one.

Starting from 1750 K, the PO^+ ion was identified in the mass spectrum of vapor over hydroxyapatite with an appearance energy of 9.1 eV. At a higher temperature, 1800 K, Ca^+ ions were also found in the mass spectrum with an appearance energy of 6.2 eV. During the isothermal exposure of the sample at 1840 K, the intensity of the PO^+ ion current gradually decreased, while the Ca^+ ion current remained constant within the measurement error. When the temperature was steadily increased to 1930, 2080, and 2200 K, in mass spectrum of the vapor over $Ca_{10}(PO_4)_6(OH)_2$ the intensity of the PO^+ ion current steadily decreased, while that of the Ca^+ ion current increased. In those cases when the intensity of the Ca^+ current was high, the CaO^+ ion was also observed in the mass spectrum, whose intensity did not exceed 1% of the intensity of the Ca^+ ion current. The obtained dependences of the PO^+ and Ca^+ ion currents in the mass spectrum of vapor over the initial hydroxyapatite sample on the evaporation temperature and time are given in the Table 1.

RESULTS AND DISCUSSION

An analysis of the mass spectra of the vapor over hydroxyapatite, as well as the measured appearance energies of ions in the mass spectra of the vapor, indicate that in the temperature range 1750−2200 K, the following gaseous species are present in the vapor over $Ca_{10}(PO_4)_6(OH)_2$: PO, atomic calcium, and oxygen. It was shown that the appearance energies of PO^+ and Ca^+ ions in the mass spectrum of vapor over $Ca_{10}(PO_4)_6(OH)_2$, determined in this work, within the measurement error of ±0.2 eV coincide with the ionization energies of PO and atomic calcium [18].

The partial pressures of the vapor species over the sample were determined by comparing the ion currents according to the equation

$$p_i = p_s \frac{I_i^+ T_i \sigma_s \gamma_s}{I_s^+ T_s \sigma_i \gamma_i}, \quad (1)$$

where p_i is the partial pressure of the ith vapor species (Pa); I_i^+ is the ion current intensity in the mass spectrum of vapor over the test substance (arb. units); T is the temperature (K); σ_i is the ionization cross section of the ith vapor species; and γ_i is the secondary electron multiplier coefficient for the ith ion. The vapor pressure over gold was chosen to be the partial pressure standard (p_s), as recommended by IUPAC [19].

The ionization cross sections of gold, phosphorus, and calcium were chosen according to the data given in [20]. The PO ionization cross section was taken in accordance with the recommendations of [21] and

Table 1. Dependence of the intensities of PO^+ and Ca^+ ion currents in the mass spectrum of vapor and of the partial pressures of the vapor species over hydroxyapatite on the evaporation temperature and time

τ, min	T, K	I_i^+, arb. units		p_i, Pa	
		PO^+	Ca^+	PO	Ca
0	1800	51	0.6	0.57	0.002
2	1820	84	0.6	0.95	0.002
5	1844	96	0.7	1.10	0.002
10	1838	99	0.6	1.13	0.002
15	1839	96	0.6	1.10	0.002
20	1839	96	0.6	1.10	0.002
30	1839	93	0.7	1.06	0.002
50	1832	69	0.6	0.78	0.002
60	1839	63	0.6	0.72	0.002
70	1841	60	0.6	0.68	0.002
75	1854	27	3.3	0.31	0.013
80	1850	42	2.4	0.48	0.010
90	1841	48	1.8	0.55	0.007
100	1838	42	2.1	0.48	0.008
110	1842	39	2	0.44	0.008
120	1850	30	3	0.34	0.012
122	1913	150	11	1.78	0.045
125	1922	110	14	1.31	0.058
130	1931	111	26	1.33	0.109
140	1933	111	45	1.33	0.189
150	1933	90	36	1.08	0.151
160	1953	108	39	1.31	0.160
170	1948	105	36	1.27	0.157
180	1953	105	36	1.27	0.153
185	2081	510	330	6.61	1.493
190	2071	102	111	1.31	0.500
200	2076	2.7	75	—	0.338
201	2198	—	840	—	4.014
205	2195	—	450	—	2.14
210	2190	—	480	—	2.28
220	2190	—	220	—	1.04
225	2190	—	140	—	0.66
230	2190	—	120	—	0.57
230	2356	—	400	—	2.04
240	2356	—	0	—	0

τ is the evaporation time, I_i^+ is the intensity of the ion current, and p_i is the partial pressure of the vapor species.
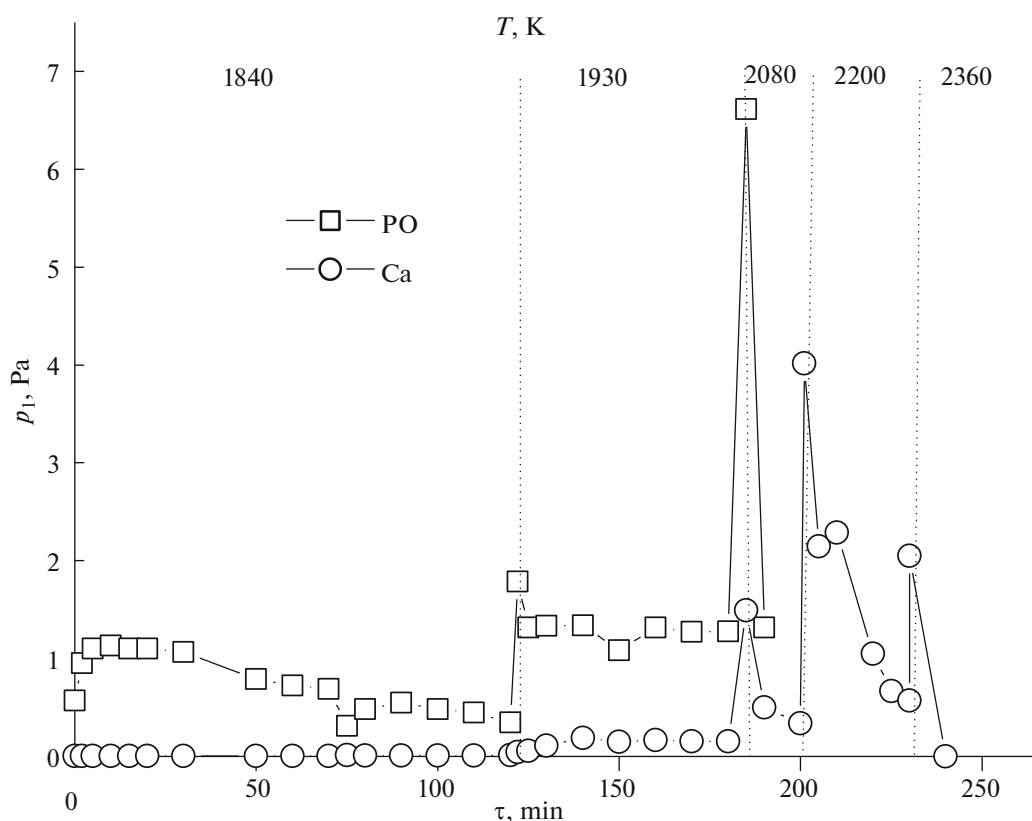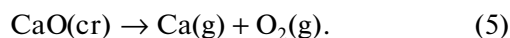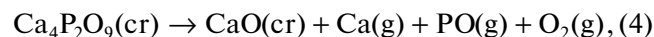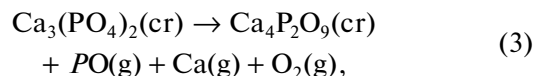
Fig. 2. Dependences of the partial pressures of the vapor species over hydroxyapatite on the evaporation temperature and time.

amounted to $0.65\sigma(Ca)$. The obtained partial pressures of the vapor species over hydroxyapatite depending on the evaporation time with increasing temperature are given in the Table 1 and Fig. 2.

The experimental data found as a result of complete evaporation of a hydroxyapatite sample suggest that when the sample is heated to $1200-1300$ K, water is removed, and hydroxyapatite is converted into calcium monophosphate $Ca_3(PO_4)_2$ by the reaction [22]:

$$Ca_{10}(PO_4)_6(OH)_2(cr) = 2Ca_3(PO_4)_2(cr) + Ca_4P_2O_9(cr) + H_2O(g). \quad (2)$$
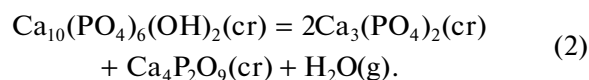
Calcium monophosphate, in turn, forms vapor starting from 1750 K according to the following reaction schemes:

$$Ca_3(PO_4)_2(cr) \rightarrow Ca_4P_2O_9(cr) + PO(g) + Ca(g) + O_2(g), \quad (3)$$

$$Ca_4P_2O_9(cr) \rightarrow CaO(cr) + Ca(g) + PO(g) + O_2(g), \quad (4)$$

$$CaO(cr) \rightarrow Ca(g) + O_2(g). \quad (5)$$

The obtained qualitative and quantitative characteristics of hydroxyapatite evaporation at 1800 K and higher completely coincide with the known processes of transition of calcium monophosphate to the gas phase, which were studied in detail earlier [23, 24]. It should also be emphasized that the results of the high-temperature mass spectrometric study of hydroxyapatite evaporation processes up to a temperature of 2200 K, performed in the present study for the first time, do not contradict the previously obtained results found by DTA at temperatures below 1473 K in [12, 15].

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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