CRS AMT2013

The 12th China–Russia Symposium on Advanced Materials and Technologies

Передовые металлы, керамические и композиционные материалы

ADVANCED METALS, CERAMICS AND COMPOSITES

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先进金属、陶瓷与复合材料

"第十二届中俄双边新材料新工艺国际会议"论文集

PART I

Edited by
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Synthetic Struvite and Newberyite Powders for Resorbable Ceramic Materials

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***Abstract*—Using the water solutions of magnesium chloride and diammonium hydrogen phosphate, disodium hydrogen phosphate and dipotassium hydrogen phosphate with a defferent sequence of pouring decantations to obtain an nanosize hydrous magnesium phosphates powders. All the synthesized powders can be used as precursor powders for the ceramic material comprising magnesium pyrophosphate phase. Getting ceramics from these powders for further study its properties in vivo and in vitro.**

I. INTRODUCTION

In the modern world, considerable attention is paid to thedevelopment of ceramic materials for medical purposes. These materials are used for the reconstruction of bone defects resulting from the pathological changes in body tissues, major surgery or trauma. According to the actual regenerative approach the emphasis is placed upon the replacement of the ceramic material with the native biological material of the growing bone. The ceramic material plays the role of an active source of many chemical elements, which are essential to new bone building a new bone.

Magnesium ion is animportant factor for bone metabolism, for the bone matrix formation and its mineralization. It can also affect the activity of osteoblasts and osteoclasts, i. e. the rate of bone growth. Therefore it is important to create materials, which contain phases that are capable of to highlight magnesium ions in the process of dissolving. Such ceramic materials can be made from powder mixtures of different calcium and magnesium phosphates such as dimagnesium phosphate or magnesium pyrophosphate. To obtain the resorbable ceramic material based on magnesium pyrophosphate with the ratio of Mg/P = 1, a method for preparing powder precursor of this phase has to be develop. Newberyite ($MgHPO_4 \cdot 3H_2O$) and struvite ($(NH_4)MgPO_4 \cdot 6H_2O$) provide an example of such powder precursors with the ratio of Mg/P = 1.

Newberyite can be synthesized according to an exchange reaction between magnesium chloride and diammonium hydrogen phosphate, disodium hydrogen phosphate and dipotassium hydrogen phosphate. The formation of struvite is also possible during the reaction of magnesium chloride and ammonium hydrogen phosphate. When heating, the synthesized magnesium phosphate which are mentioned before transform into magnesium pyrophosphate (1-3).

$$2MgHPO_4 \cdot 3H_2O \rightarrow Mg_2P_2O_7 + 7H_2O \quad (1)$$

$$NH_4MgPO_4 \cdot 6H_2O \rightarrow NH_4MgPO_4 \cdot H_2O + 5H_2O \quad (2)$$

$$2NH_4MgPO_4 \cdot H_2O \rightarrow Mg_2P_2O_7 + 2H_2O + 2NH_3 \quad (3)$$

Some of the by-products of synthesis of dimagnesium phosphate due to its ability to decompose on heating with formation of volatile species can be attributed to the group of removable during heat treatment (drying, calcination) by-products. Choosingmagnesium chloride and diammonium hydrogen phosphate, disodium hydrogen phosphate, dipotassium hydrogen phosphate as starting materials is attractive because the associated by-products of the reaction (sodium chloride, potassium chloride, and ammonium chloride) can leave the synthesized powder immediately drying storage, during or heat treatment. Thermal instability of ammonium nitrate suggests that its impact on the process of thermal conversion of magnesium phosphate into magnesium pyrophosphate will not be significant. Such by-products as potassium or sodium chloride can also be removed from the powder preform, but only after reaching the melting temperature of these salts. These salts exhibit fairly high volatility after reaching the melting temperature.

The aim of this work was to obtain synthetic powders forthe fabrication of ceramic material with the phase composition, which is mainly comprised of magnesium pyrophosphate. Magnesium phosphate powder was synthesized from magnesium chloride and diammonium hydrogen phosphate, disodium hydrogen phosphate and dipotassium hydrogen phosphate. The following tasks were solved to achieve the goal: 1) synthesis of hydrous magnesium phosphates (newberyite or mixture of newberyite and struvite) and 2) the investigation of the properties of the synthesized powders according to the reacrions (4–6).

Ⅱ. EXPERIMENTAL

Synthesis was carried out according to reactions 4–6 by means of two ways. Firstly 400 ml of hydrous $(NH_4)_2HPO_4/K_2HPO_4/Na_2HPO_4$ with the concentration 1M were added to 400 ml of 1M concentration water solution of $MgCl_2$. Then the water solution of $MgCl_2$ was added to water solution of $(NH_4)_2HPO_4/K_2HPO_4/Na_2HPO_4$.

$$(NH_4)_2HPO_4 + MgCl_2 + xH_2O \rightarrow MgHPO_4 \cdot 3H_2O/NH_4MgPO_4 \cdot 6H_2O + NH_4Cl \quad (4)$$

$$Na_2HPO_4 + MgCl_2 + 3H_2O \rightarrow MgHPO_4 \cdot 3H_2O + 2NaCl \quad (5)$$

$$K_2HPO_4 + MgCl_2 + 3H_2O \rightarrow MgHPO_4 \cdot 3H_2O + 2KCl \quad (6)$$

After stirring the suspension for 10 minutes the precipitate was separated from the mother liquor on a Buchner funnel using a vacuum pump. After dryingof sludge in a thin layer for a week the product was disaggregated in acetone for 5 minutes with the ratio of "acetone powder: grinding bodies" equal to 1:1:5. After disaggregation and evaporation of acetone the powder was sieved (the mesh size was 200 μm).

Paraffin was used as a temporary binder. Paraffin at the rate of 10% wt in the from of solution in CCl_4 was added to the powder of hydrated dimagnesium phosphate. Samples in the form of discs, which are 12 mm in diameter and 3–4 mm in height, were formed at the pressing pressure of 50 MPa.

Samples in the form of discswere annealed in the range of 800–1100 ℃ at a heating rate of 5°/min with the exposure at the final temperature for 2 hours.

X-ray diffraction studies were carried out on a D/MAX-2500 Rigaku diffractometer (Japan) with a rotating anode using Cu *Kα* radiation (angular range $2\theta = 2-60°$ with the increment 0.02°, the speed of spectra recording 5°/ min).

The electron microscopic study was carried out using a field-emission Supra 50 VP Carl Zeiss scanning electron microscope (Germany) at accelerating voltages of 20 kV. This study makes it possible to distinguish sample areas with different chemical composition.

Ⅲ. RESULTS

The powder X-ray diffraction data (Fig. 1) obtained in a different order of adding of the reagents (magnesium chloride to potassium hydrogen phosphate, sodium hydrogen phosphate, ammonium hydrogen phosphate and vice versa), indicate that each powder consists of newberyite ($MgHPO_4 \cdot 3H_2O$) and/or struvite ($(NH_4)MgPO_4 \cdot 6H_2O$).

In the process of draining of magnesium chloride, potassium phosphates, sodium, ammonium particles have large dimensions than the reverse (Fig. 2).

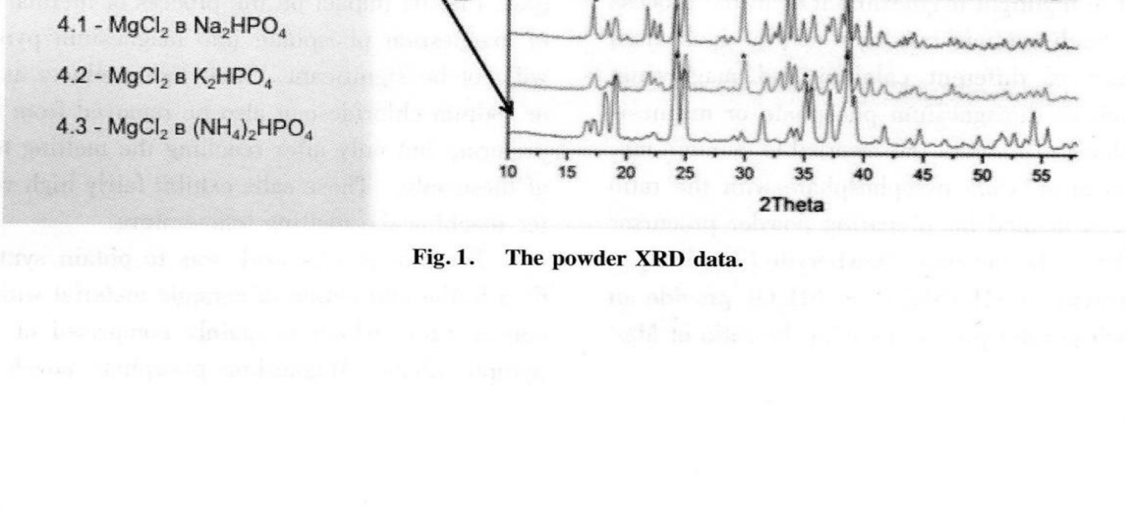

Fig. 1. The powder XRD data.

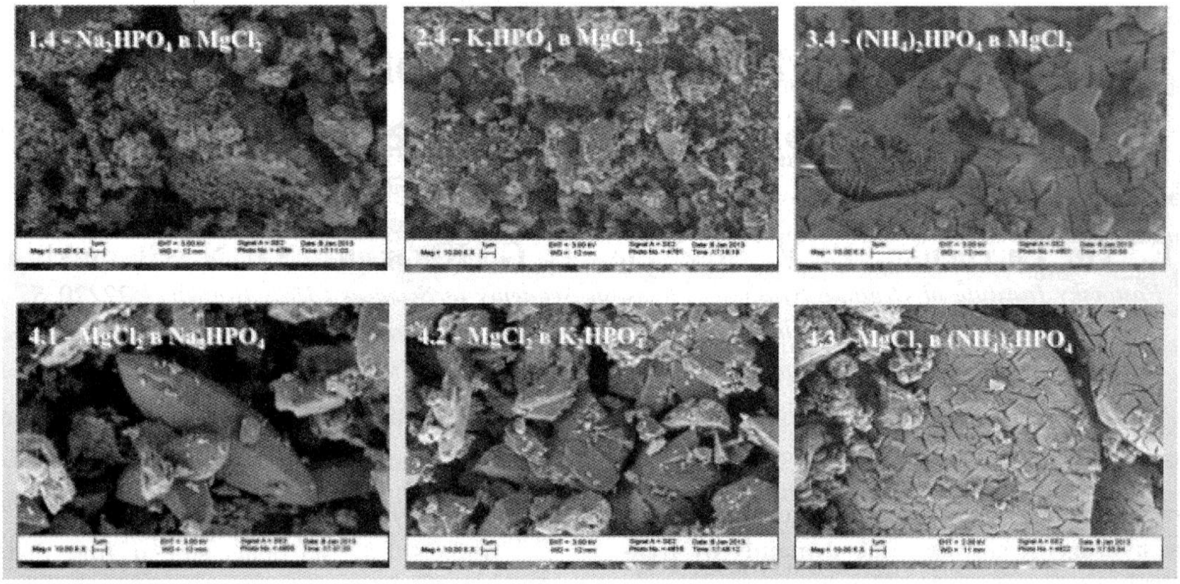

Fig. 2. The microstructureof powders.

Ⅳ. CONCLUSIONS

Water solutions ofmagnesium chloride and diammonium hydrogen phosphate, disodium hydrogen phosphate and dipotassium hydrogen phosphate with a defferent sequence of pouring decantations make it possible to obtain an nano-sized hydrous magnesium phosphates powders (newberyite or mixture of newberyite and struvite). Newberyite ($MgHPO_4 \cdot 3H_2O$) and struvite ($(NH_4)MgPO_4 \cdot 6H_2O$) provide an example of such powder precursors with the ratio of Mg/P = 1. All the synthesized powders can be used as precursor powders for the ceramic material comprising magnesium pyrophosphate phase. In the process of draining of magnesium chloride, potassium phosphates, sodium, ammonium particles have large dimensions than the reverse. The present work develops the idea of getting resorbable ceramics, which contain phases that are capable of to highlight magnesium ions in the process of dissolving from synthetic struvite and newberyite powders.