Development of the technology of obtaining the composite based on the "magnesium-bone substance" for biodegradable implants by the method of powder metallurgy

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Abstract. This work reports on the development of a composite "magnesium (Mg)- bone substance (HA)" for a biodegradable implant using powder metallurgy methods. In the course of the work, experiments were performed in two different types of a powder compaction: sintering this composite by standard compaction method and the spark-plasma sintering method (SPS). The optimum parameters for compacting the powder mixture were selected, the initial percentage of open porosity after sintering samples was calculated, X-ray microanalysis was performed, and the microstructures of the samples, which had been obtained by using various powder metallurgy methods, were compared.

1. Introduction
Sometimes, surgical intervention leads to extensive postoperative defects and, as a result, to functional insufficiency of the musculoskeletal system. A traditional approach is to replace a bone defect with an implant. The main purpose of this developing direction is the creation of an implant material, which must appropriate the following requirements:

- biocompatibility;
- bioactivity;
- corrosion resistance;
- strength.

Magnesium (Mg) exhibits excellent biocompatibility with the human body, the strength properties are still similar to the human bone strength properties, that is way, Mg is a perspective material for creating biodegradable implants. However, its corrosion performance at the current stage of development is still not good enough for increasingly diverse practical applications [1]. Thus, in order to reduce the corrosion rate and increase the time of implant degradation until the bone tissue is fully restored, various approaches are being discussed [2-7]. On the one hand, the authors of [2-6] propose to increase the corrosion resistance of magnesium implants by creating alloys - adding to magnesium alloying elements such as: Al, Zn, Mn, Zr, Gd, Sr. On the other hand, to prolong the time of implant degradation helps purification of magnesium from harmful impurities and anodizing, proposed [6]. In addition, to temporarily slow down the decomposition, appropriate types of coatings can be applied to the surface of a magnesium implant [7].

All approaches are promising, but at the present moment, none of them has yet led to the creation of commercially available products, the reason for this is not the full compliance of the implant material with the requirements. Regardless of the efforts undertaken, there is a real demand for
solutions that allow realizing the production of biodegradable magnesium implants for the needs of traumatology, orthopedics and surgery.

Considerable efforts were directed to the development of ceramic materials based on Calcium hydroxyapatite (HA, \( \text{Ca}_{10} \left( \text{PO}_4 \right)_6 (\text{OH})_2 \)) - it is an analog on the phase and chemical composition of the mineral component of human bone tissue [8-11]. Materials based on HA do not have a negative impact in the human body, unlike a number of metals and polymers, and biologically active in relation to the formation of bone apatite. But the known hydroxyapatite ceramic materials have rather low mechanical characteristics in order to perceive physical exertion in many necessary situations with a high degree of reliability.

We have attempted to create a porous composite based on HA with reinforcing substance-magnesium (Mg) in the matrix of the material. To retain the initial properties- bioactivity of hydroxyapatite and biodegradability of magnesium, and close values of the strength characteristics with bone tissue, this composite can only be obtained by using powder metallurgy methods.

Some authors [12-14] reported the presence of magnesium (Mg) in calcined living tissues, which would indicate that Mg-ions could improve the biocompatibility and bioactivity of CaP ceramics [14-15]. Magnesium is one of the essential elements for all living organisms, approximately 60-65% of the total amount of Mg is in the human body- in the teeth and bones, and the remaining 35-40% is in the soft tissues, organs and blood. Mg is involved in important functions of the body, for example, it stimulates the muscle activity of the heart muscle, thereby helping to maintain a stable heart rate [16]. Mg, as well as Ca, provides strong and healthy bones, reducing the risk of osteoporosis. Osteoporosis of beneficial micronutrients from bone tissue is caused by a deficiency of Mg [17]. It is expected that implants based on the composite “magnesium (Mg)- bone substance (HA)” will contribute to restore the bone, provide faster and more efficient regeneration of the damaged bones area. In the process of degradation of the implants in body medium gradually releasing Mg\(^{2+}\) cations, stimulating the appearance of osteocyte bone cells [18]. Physical and chemical properties of the material guarantee progressive process of bone regeneration until it is completely will be replaced by new bone.

In the conditions of the modern world and rapidly developing technologies, the goals of this development are not just to reduce the corrosion rate of implants and increase the strength of the composite obtained by powder metallurgy methods, but to create such a material that will increase the rate of bone splicing, the time of bone tissue regeneration, contributing to the formation of healthy callus by replacing the implant with live bone tissue.

2. Experimental procedure

2.1 Sample preparation

The initial powders of magnesium and hydroxyapatite were investigated; the particle size distribution was carried out on a laser particle analyzer ANALYSIS22. Visually, magnesium powder has a silver color, and HA powder has a pure white color. The analysis showed the average particle size of magnesium is 100\(\mu\)m, the size of agglomerates of synthetic HA powder obtained by the sol-gel method was 80\(\mu\)m, but the powder itself is fine dust with nanoscale particles. The pycnometric density of these powders was measured at the Helium pycnometer- AccuPyC II 1340. The density of magnesium powder is 1,729 g/cm\(^3\), which is consistent with the theoretical density, the density of HA is 3,472 g/cm\(^3\). Using a Jeol JSM scanning electron microscope, an image of the particles was obtained, which could be used to determine their shape (figure 1-2):
Pure powders of the following components were prepared: HA and Mg; the mixture was mixed by a mechanical activation method; grinding of powders in a ML-1 ball vibratory mill. The mixture consisted of 9g HA and 1g Mg (volume ratio of 70% HA and 30% Mg), steel cups with steel balls were used; grinding was carried out in an Ar atmosphere in order to exclude the formation of magnesium oxide. Duration of grinding was 15 minutes. The size and shape of the powder particles after grinding is presented in figure 5.

**Figure 1.** The size and shape of magnesium powder particles (magnification × 500).

**Figure 2.** The size and shape of the particles of hydroxyapatite powder (magnification × 500).

**Figure 3.** The size and shape of the particles of the mixture of the starting components after grinding in an argon atmosphere (magnification × 500).
As can be seen from the above figure, the size of the mixture after grinding average 8μm, but there is also an area with nanoscale particles.

2.2 Sintering of the composite by the traditional powder method

The first step in the experiment was to check the possibility of obtaining the composite “Mg-HA” using the standard powder metallurgy method — pressing and free sintering. Two batches of tablets were prepared: the ratio of the volume fractions of the components of 70% HA and 30% Mg. The sample sintering experiment was carried out in an argon (Ar) atmosphere and in a high vacuum in a furnace.

Previously, preliminary sintering tests were carried out on Mg- it was found that the optimal sintering temperature is about 500°C, at this temperature the samples would not crack, not form cracks, there would no gradient from the tablet to the center, sintering occurred throughout the volume evenly. The tablets were compressed in an Ar atmosphere, the applied pressure was 25MPa. The electronic image of the structure of the obtained samples is shown in figure 4.

**Figure 4.** Electron image of the microstructure of the sample of composite “Mg-HA” obtained by standard powder method: (a) obtained in the mode of back-scattered electrons with magnification × 100, (c) with magnification × 500, (b) obtained in the mode of secondary electrons with magnification × 100, (d) at magnification × 500.
The microstructure of the composite, obtained by the standard powder metallurgy method, has a different morphology and grain size, the interphase boundaries are poorly defined, there are cracks passing both along the grain boundaries and intersecting them. The magnesium particles are unevenly arranged in the ceramic matrix. Therefore, in practice, the problem arises of preserving the structure of compacts before sintering, i.e. prevent intensive agglomeration of particles at high pressing pressures in order to preserve nucleation centers and prevent grain growth during sintering. The dispersion of powders has a much greater effect on their compactibility than their physical and mechanical properties. Table 1 presents data on the density of the samples before sintering and after.

| Sample 1 | Sample 2 |
|----------|----------|
| Σρ, g/cm³ | 2.95     | 2.95     |
| ρgeo(before), g/cm³ | 1.82     | 1.94     |
| ρgeo(after), g/cm³ | 1.72     | 1.65     |
| ρpic, g/cm³ | 2.2      | 2.1      |
| % open.por. | 16.3     | 16.9     |

Traditional methods of static pressing lead to the formation of an inhomogeneous structure, grain growth in the compaction process and a not sufficiently high density of compacts. A promising method that can offer an alternative solution to these problems is electropulse compacting of powders - spark-plasma sintering (SPS).

2.3 Sintering of the composite by the SPS method

The second step in the experiment was to test the possibility of obtaining a composite “Mg-HA” using the spark-plasma sintering method. For this, a mechanically activated mixture was prepared; it was poured into a graphite matrix of 10mm in size, with graphite paper and tungsten foil, in order to eliminate interaction with graphite. Sintering parameters at the LABOX-152VHD unit: -500°C heating 20°C per minute, pressure-25MPa, holding time-10 min. At this stage, two mixtures of this composite with 70% HA-30% Mg by weight and 70% HA-30% Mg by volume were sintering to determine the effect of the amount of reinforcing substance (Mg) on the structure of the composite as a whole and the effect of the relative amount of HA on porosity of the obtained samples after sintering. The microstructure of the samples is shown in figure 5. Magnesium particles are more elongated and rounded grains, evenly spaced in a porous ceramic matrix, the interphase boundary is clearly visible:
Figure 5. Electron image in the back-scattered electrons of the microstructure of the sample of the composite “Mg-HA” obtained by the SPS method: a) the composition of the composite is 70% HA-30% Mg by mass, magnification × 100; b) the composition of the composite is 70% HA-30% Mg by volume, magnification × 100; c) 70% HA-30% Mg by weight with magnification × 500; d) 70% HA-30% Mg by volume with magnification × 500.

3. Results and discussion
During the experiment on sintering the composite “Mg-HA” by the standard powder metallurgy method, it was found that a batch of compressed tablets after sintering in an Ar atmosphere, did not sinter, due to the long duration of the process, the decomposition of HA and the color change of the tablets is observed on thr figure 6:

Figure 6. Batch of composite samples: (a) prior to sintering in an Ar atmosphere, (b) after sintering in an Ar atmosphere.

One of the important stages in the technology for producing a composite is the study of its structural phase state; for this purpose, an X-ray microanalysis was carried out on a Jeol JSM microscope of composite samples of a “Mg-HA” obtained by various powder compaction methods.
Figure 7. Map of elements on the plot of the composite 70% HA-30% Mg by volume: a) section of the surface of the ground section chosen for distribution of the elements; b) magnesium excretion.

Figure 8. The total spectrum of chemical elements on the plot of the composite 70% HA-30% Mg by volume, obtained by the SPS method.

Figure 7 (a) illustrates a section of a 70% HA-30% Mg composite by volume obtained by the standard powder metallurgy method; from the chemical element maps (b), it can be seen that the particles are distributed in the composite matrix are magnesium particles. The total distribution spectrum of the chemical elements shown in figure 8; the spectrum was detected insignificant potassium content.

According to the results of micro X-ray spectral analysis of the composite section sintered by the SPS method (figure 9), it can be seen that this composite is represented by two phases, large grains are magnesium- evenly spaced in a matrix consisting of elements such as phosphorus, calcium, oxygen. The boundaries of the diffusion interaction of magnesium and hydroxyapatite have not been identified, it can be concluded that at this sintering temperature does not the interaction between components, new phases are not formed. Thus, the mapping of the selected surface area can be very informative and widely used in the analysis of surface areas of both metal and composite samples.
Figure 9. Map of elements on the plot of the composite 70% HA-30% Mg by volume, obtained by the SPS method: (a) the plot of the surface selected for distribution of the elements; (b) Magnesium distribution; (c) Oxygen distribution; (d) Phosphorus distribution; (e) Calcium distribution.

4. Conclusions
This study focused on the development of a composite "magnesium (Mg) - bone substance (HA)" for a biodegradable implant using powder metallurgy methods. During the experiments, the following conclusion was drawn: it is necessary to significantly speed up the sintering process of the composite in order to exclude its interaction at all stages of the technology with the atmosphere and prevent
decomposition of HA. A perspective option is the use of electro-pulsed methods of compaction, namely the use of SPS method.

Based on the experiments performed on sintering the composite using various powder metallurgy methods, the optimum compaction parameters were established and the initial open porosity was calculated after sintering the samples (table 2-3).

| Method      | $\Sigma \rho$, g/cm$^3$ | $\rho_{geo}$, g/cm$^3$ | $\rho_{pic}$, g/cm$^3$ | $\%_{geo}$ | $\%_{relative}$ | $\%_{open.por}$ |
|-------------|------------------------|------------------------|------------------------|------------|------------------|-----------------|
| SPS         | 2.9                    | 1.72                   | 2.1                    | 58.4       | 71.9             | 13.5            |
| Free sintering | 2.9                | 1.71                   | 2.2                    | 58.2       | 75               | 16.8            |

Bone tissue is one of the types of connective tissue consisting of three types of cells and the extracellular matrix. The cells make up 1-2% of the total volume of bone tissue, the rest of the volume is occupied by pores and channels (for compact bone tissue, the porosity is 13-18%, for spongy it is higher) and the solid phase is organic and mineral components of bone plates. The organic component (40-50% of the solid phase) is represented by collagen. The mineral component (50-60% of the solid phase) is predominantly the crystals of hydroxyapatite $\text{Ca}_{10} (\text{PO}_4)_6(\text{OH})_2$ and other calcium salts. Thus, it can be concluded that the composite “Mg- HA” obtained by powder compaction methods has a close initial porosity to the porosity of compact bone tissue, which is a good indicator for increasing the speed of bone growth in the composite and, therefore, accelerating regeneration.

| Table 3. The optimal parameters of compaction of the composite |
|---------------------------------------------------------------|
| Parameters of compaction | Values |
| Pressing pressure, MPa | 25 |
| Sintering temperature, $^\circ$C | 500 |
| Holding time, min. | 10 |

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