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## **POROUS MATERIALS USED AS INSERTED BONE IMPLANTS**

### **Review Paper**

#### **ABSTRACT**

The materials being in use in medicine require some improvement, as well as new materials are needed. One of the newest trends in the development of implants, is applying the porous structures – scaffolds, which are expected to produce vesseled bone tissue at a quicker rate and a stable joining of implant with the body. The aim of the paper is the review of porous materials in the latest literature.

**Key words:** *porous materials, bone implants*

#### **INTRODUCTION**

Every implant introduced into the body is an alien body and causes a defence from immunological system in the form of allergies or inflammation. Consequently it may occur that the implant is rejected.

According to many scientists using the porous materials enables mechanical joining of the implant with the regular tissue through the ingrowing into the introduced item. The size of pores and connections between them influence the process of penetration and mineralization of tissues, giving as a result proper and constant joining of the implant and the bone [1,2]. Additional feature of porous materials is Young's modulus significantly lower than modulus of bulk metals, like the bone. Decreasing of implant stiffness ensures proper stress distribution in the implant – bone system, hence enables conditions to bone restoration and allows to avoid the problems associated with stress shielding [3-5].

Rajzer and other scientists created a specific type of three dimensional fibrous structure made of fibres differing in diameters and porosity (micro – and nanopores). These materials will form a 3D scaffold containing fibrous components, which imitate the structure typical of natural tissues. The prepared material contains two types of pores:

1. pores between fibres in which cells could penetrate growth and proliferate to promote the formation of tissue and
2. pores in the fibre microstructure. Porous carbon fibres used as a scaffold for tissue regeneration could simultaneously serve as a support for the delivery of drugs or biologically active agents, which would stimulate tissue growth.

The in vitro cytotoxicity tests revealed that the direct contact of the human body with porous carbon fibres did not show any cytotoxicity effect [6].

In recent years a great interest has been aroused by the so – called new generation of bioactive materials with increased bioactivity, interpreted mainly as the ability to simulate alive tissue to faster regeneration. To produce materials of this type, the chemical sol – gel method is used. It enables to obtain biomaterials of high chemical and biological surface activity. This method allows to produce biomaterials in the form of powders, granules, dense and porous sinters as well as thin coatings on bionatural substrates [7-10].

In case of such materials, through proper choice of the chemical composition of the initial powders and the sintering conditions, there exists the possibility to fabricate implants, which become firmly fixed in the parent tissue both biologically (the tissue is penetrated by the porous structure) and chemically (combined with the parent tissue through a layer of hydroxyapatite, crystallizing on the surface of the biomaterial) [7].

### SCAFFOLDS

Tissue engineering aims at replacing or sustaining the functions of tissues and body organs (damaged in trauma or inborn diseases) by means of implants, which contain the patient's cells, fixed to three dimension bases [10]. The basic material is of major importance in the process of creating new tissues. The scientists [8-10] showed, that tissue renewing and restoring depends on the microstructure of the material used as a cell scaffold. It is believed that the best results in bone cells bred in vitro can be achieved in case of 100-400  $\mu\text{m}$  pore size [10-12]. The best breeding basis for tissue engineering are those with the biggest open porosity. It enables to place the largest amount number of cells and intensify the process of vein penetrating. The porous basis must keep its microstructure for the period necessary to form a new tissue. It is supposed to crush, collapse and deform excessively, which might cause the destruction of the tissue, which is being formed [10].

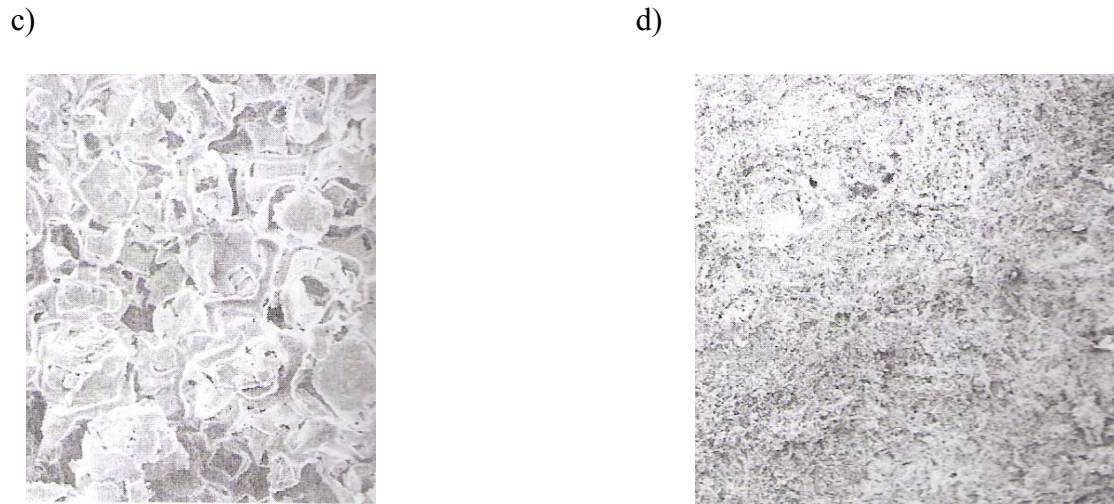
Pamula [13,14] and some other scientists used the breeding basis with the special size of pores: 600  $\mu\text{m}$ , 500  $\mu\text{m}$ , 200  $\mu\text{m}$ , 40  $\mu\text{m}$  to receive degradable biomaterials (Fig.1). In all cases the porosity was 87%, that is bigger than expected. The porous basis preserved its size and structure both in the air and in water. It was found that the durability of porous basis degradation depends on chemical structure and can be easily controlled [10].

a)



b)





**Fig.1.** Scanning electron micrographs of PGLA porous scaffolds with different size of pores: a) 600 µm, b) 500 µm, c) 200 µm, d) 40 µm [10]

The use of three dimensional scaffolds settled with cells and next implanted into the place of tissue loss creates good conditions for the tissue regeneration. The aim of porous implants – foams is to support the three dimensional tissue formation [15]. The concentration of cells is started in vitro on the porous structure of scaffold and next the obtained item is placed in the site of the tissue loss. To assure the proper growth of the tissue, the pore should be interconnected and large enough to permit cellular migration, diffusion of nutrients and metabolites and the proper angiogenesis. As the new tissue is developing the implant undergoes gradual degradation [11,15].

To obtain the porous sinters a method of sintering compounds and deposition of slip casting on a organic substrate was used. The elementary powder was mixed with various additions (dextrin, methyl, cellulose, starch) until the slip casting of appropriate consistence was obtained. In the applied method the polymeric sponge was used as a substrate (polymeric sponge method) [16].

The applied method of sintering with the application of the deposition for the slip casting on organic substrate has proved to be a good method of obtaining sinters with a favorable microstructure from the point of view of medical application (implants). When using as additions starch and methyl cellulose the authors obtained sinters characterized by open porosity reaching up to 77%, which creates advantageous conditions for the osseous tissue to grow inside the implant. At the same time, examination of the microstructure using a electron scanning microscope has shown that the newly formed pores have similar dimensions and are uniformly distributed in the whole material. The obtained sinters were characterized also by good mechanical durability, without showing a tendency to crush under the pressure [7]. Gel – the product of powdered  $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$  represent a convenient starting material for the production of porous sinters, which can be used as osseous implants [7,17,18].

The bone infections cause the significant clinical problem and in most cases they need a long antibiotic treatment. The effectiveness of the treatment could be increased by the local deposition of the antibiotics, which additionally diminish the general effect of the long lasting antibiotic treatment in human patients. Among the materials, which could be used as the effective drug carriers, especially in bone surgery, are porous corundum implants of the high biocompatibility. Paluch and other scientists [17] compared in vitro environment some porous corundum materials with some amount of new generation

antibiotics. The examination of the corundum porous biomaterials in vivo, conducted initially on rabbits and then on sheep showed that non – mineral organic substances occur already after 3 days of being in the human body, in its outer pores sticking to the bone tissue. After 6 weeks the process of filling in the pores reaches 80% and after 16 weeks the penetration of the pores and mineralization of the bone are completed (Fig.2) – the pores are filled with the bone tissue the Haver's channels and medullar wholes can be observed. It has been also shown that the bone, which is in contact with the implant, grows into the pores of the biomaterial, which enables the control over the type of bone growing into the pores [1].

Experiments carried on animals indicate, that the behaviour of corundum ceramics, as well as its matrix containing vankomicine developed in a biological accordance. After a month some tissue and cell elements were observed. It pointed to the fact that the inflammation did exist, but after 3 months the process of recovery of the surrounding bone tissue was visible. The process of bone formation was carried on, which could be seen after 6 and 9 months [19].

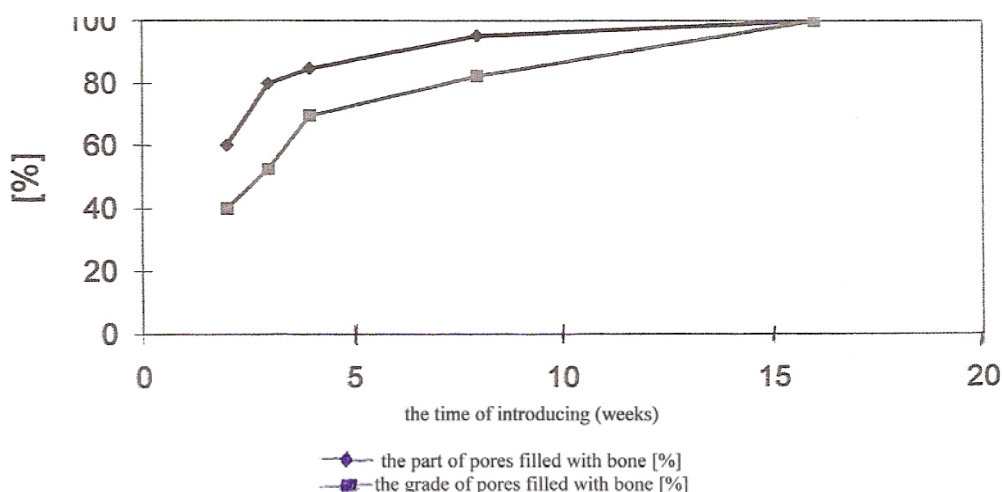


Fig.2. The grade of implant pores filled with bone tissue [1]

### HYDROXYAPATITE BIOCERAMICS

The obtaining of a suitable material, which would act as a bone implant and at the same time would fulfill the medical requirements and assure clinical success, is the field of many research works [20-23]. Hydroxyapatite is a material most resembling, from the chemical point of view, the inorganic part of bone tissue. It is obtained by chemical synthesis and it is a starting material in the process of obtaining porous ceramics. The appropriately designed ceramic porous materials are simultaneously the material resembling the spongy structure of bones, and due to the optimal selection of porosity and pore size, they permit the ingrowing of the bone tissue and more permanent connection with the bone. However, porous ceramics, and especially hydroxyapatite, are characterized by low resistance to brittle fracture, which in the case of materials intended to fulfill mechanical functions, are an important problem. The production of porous ceramics in the form of composites, i.e. combination of two or more selected phases, permits to remove these undesirable properties [22,24-26]. The introduction of

an appropriately selected organic polymer into the pores of the ceramic material leads to the obtaining of new strength characteristics of the composite. The use of biodegradable polymer permits, however, gradual ingrowing of the bone tissue into the composite pores by simultaneous degradation of the polymer, which may lead to its complete replacement by a live tissue [20,21,23,27].

So far hydroxyapatite ceramics has been widely applied to replace bone in the form of porous items. The porous, synthetic hydroxyapatite joins the bone firmly, because it connects the tissue with implant forming biological unit. It enables to place the implant into the bone, protecting it from loosening. The requirement, which must be met, so that the tissue could grow into the biomaterial pores and stay alive, is the proper size of open pores [28]. It is assumed, that the minimum size of open pores enabling the formation of biological connection between implant and bone is 100  $\mu\text{m}$ . If the pores reach the value of 200  $\mu\text{m}$ , there is a possibility of appearing osteons within the implant, which has a favourable influence on integration of the implant and bone. It can be expected, that with the proper stiffness the bone veins would grow into the pores [29-32].

The available porous hydroxyapatite implants show the bending strength from 2 to 11 MPa, the compressive strength from 2 to 100 MPa and the tensile strength about 3 MPa. The mechanical parameters of the implanted hydroxyapatite biomaterials are improved after penetrating the bone tissue. It has been shown that the pores are penetrated by the medullar bone up to 50-60%. The bending strength increased up to 40-60% MPa. The endurance parameters of porous hydroxyapatite can be improved with matrix, which consists of hydroxyapatite covering hydroxyapatite fibres. The porous hydroxyapatite material tends to show degradation. The porous hydroxyapatite bioceramics is widely used in medicine to fill in the wholes in dentistry and orthopaedics or drug conveyers [33].

Application of new bone implants based on magnesium alloys brings new possibilities in bone losses treatment [34].

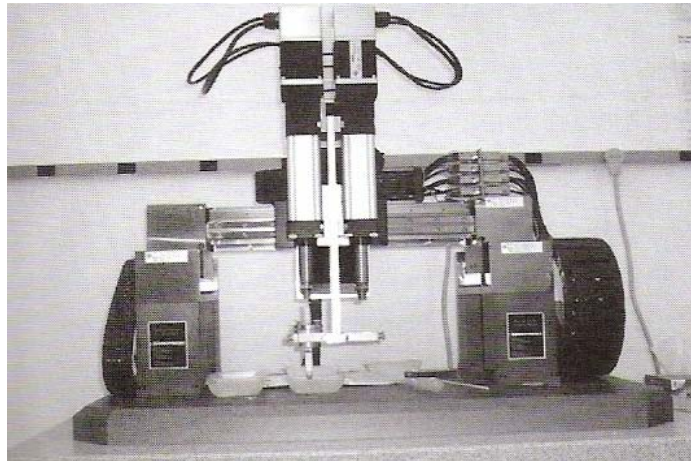
Thanks to temporal properties, revealed during operation in vivo magnesium alloys can be qualified as a bone loss filling material. Yet, due to not optimized resorption time, they are not applied in clinical conditions. One of the methods, improving this inconvenience is manufacturing hybrid structures. They have the same core, which is on magnesium alloy as a monophase material should be characterized by fair mechanical properties. The idea of monophase hybrid structure leads to linking the solid material with the open pore one with a metallic bond. Thanks to this connection, open pore properties are obtained. This allows physiologic fluids flow as well as joining with natural bone. The solid material, in turn, brings greater possibilities of building the skeleton for load bearing, enhancing the development of natural metabolism of the osseous system [34,35]. This brings new possibilities for applying the magnesium alloys, which, as temporary implants may be used in vast systems of bone fillings, not available in sponges of only porous structure so far [34-37].

## ROBOCASTING – A NEW METHOD OF POROSITY FORMING

Global medical market puts big pressure on new porous bioceramic materials discovering and elaborating together with new fabrication techniques. Many modern methods were elaborated e.g. powder sintering, chemical and mechanical foaming,

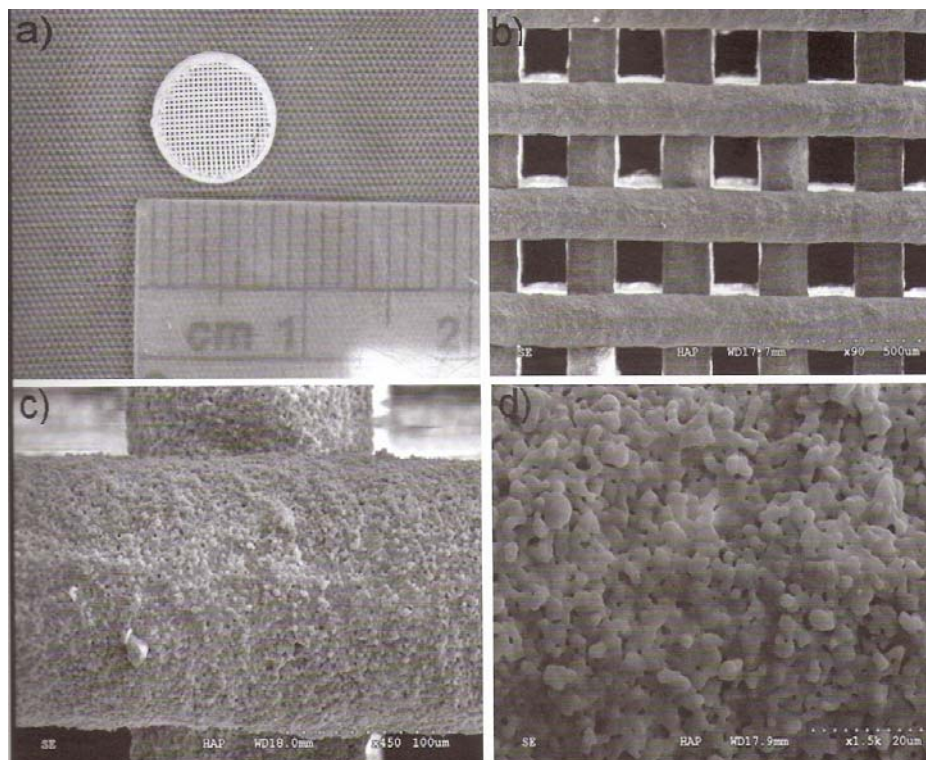


biofiltration, foam replication [38]. One of the most recent, discovered and patented, a few years ago, being still developed is “Robocasting” known also as three dimensional printing (Fig.3) [38,39]. There were trials to adapt it for ceramic powders processing [40], especially for bioceramics [38]. Early research leads to a feedstock material preparation-paste/ink, which is necessary for “Robocasting” process.



**Fig.3.** Robotic deposition device [38]

Complete manufacturing chain (printing, drying, sintering) for 3D bioceramic structures with controlled porosity was elaborated (Fig.4) [38,41]. One of many advantages of additive layer-by-layer forming is low cost of production, short production time and almost no scraps are their aptitude for arbitrary object shaping. CAD-CAM environment is used to transfer and convert data (geometry, size and shape, macrostructure) [42,43].



**Fig.4.** Hap sample by Robocasting. Macro and micro porosity is present [38]

The ideal bone substitute is a material that will form a secure bonding between implant and tissue by allowing or even encouraging new cells to grow and penetrate. From mechanical point of view the structure of such an implant should be as close to natural as possible. Strength, toughness, Young modulus etc. should correspond to natural bone properties. An ideal scaffold should have 3D interconnected porosity with pore size in the range of 100-400  $\mu\text{m}$  [39,44,45].

Plastic or reconstructive surgery is a field of potential use of such implants (neoplasm of the bone, destroyed bone tissue after injuries etc.). Individuality and uniqueness of each medical case requires the one-time-worked-out surgical procedure. By using RP techniques not only implant preparation is faster but also its quality and precision are higher. Having a Computer Tomography (CT) data (pile of scans) [46-48] it is possible to prepare one-and-only, absolutely fitted in shape, personalized implant [39,44-49].

## CONCLUSIONS

The structural-adaptive compatibility of bone-porous implant fixation concerns ability of porous coating to induce the effective bone tissue ingrowth into its pores allowing bone mineralization. This ability is characterized by the structural osteoinductive properties of porous coating of implant and guarantees the proper bone-implant fixation. The osteoinductive properties of porous coating are determined by the proper parameters of its microstructure.

While introducing the implant into the human body an assumption is made that its functional durability will be long. Good implant – bone connection and a proper shape of the implant adapted to the placement of the tensions on the tissue – implant verge enabling stiff position of the implant into a bone throughout the whole period of its stay in the body, will make it possible to create the conditions typical of healing of a broken bone. It is a task for the porous structures. The scaffolds accelerate the process of producing the bone tissue, causing better location of the implant in the human body.

## REFERENCES

1. Rosiek G., Misiewicz C., Bieniek J.: Behaviour of a corundum porous material in a living organism – Part I – Glass and Ceramics (*Acta Ceramica*), 2, 1984, 41-44.
2. Ryan G., Pandit A., Apatsidis D.P.: Fabrication methods of porous metals for use in orthopaedic applications. *Biomaterials* 27 (2006), 2651-2670.
3. Gradzka-Dahlke M.: The effect of structure on mechanical properties of porous sinters made of implant steel 316L. *Engineering of Biomaterials*, X, 65-66, 2007, 17-19.
4. Takemoto M., Fujibayashi S., Neo M., Suzuki J., Kokubo T., Nakamura T.: Mechanical properties and osteoconductivity of porous bioactive titanium. *Biomaterials* 26, 6014 – 6023 (2005).

5. An Y.B., Lee: Synthesis of porous titanium implants by environmental–electro–discharge–sintering process. *Materials Chemistry and Physics* 95, 242-247 (2006).
6. Rajzer I., Blazewicz M., Menaszek E., Czarny A., Zaczynska E.: The effect of the carbon fibres diameter on cell response. *Engineering of Biomaterials*, X, 67-68, 2007, 52-56.
7. Sindut R., Laczka M., Cholewa – Kowalska K., Najman J., Szymonska J.: Porous bioactive sinters. *Engineering of Biomaterials*, VIII, 45, 2005, 16-23
8. Ma P.X.: *Materials today*. 2004, 7 (5), 30-40.
9. Seal B.L., Otero T.C., Panitch A.: *Materials Science and Engineering*, 2001, 34, 147-230.
10. Pamula E., Buczynska J., Menaszek E., Bacakova L., Dobrzyński P., Bero M.: Resorbable porous scaffolds for tissue engineering. *Chemik* 2/2005, 57-62.
11. Yang S., Leong K.F., Du Z., Chua C.K.: *Tissue engineering*. 2001, 7, 679-689
12. Frosh K.H., Bravencik F., Lohmann C.H., Viereck V., Siggelkow H., Breme J., Dresing K., Strurmer K.M.: *Cell Tissue Organs* 2002, 170, 214-227.
13. Pamula E., Blazewicz M., Czajkowska B., Dobrzyński P., Bero M., Kasperczyk J.: Elaboration and characterisation of biodegradable scaffolds from poly (L-lactide-co-glycolide) synthesized with low-toxic zirconium acetylacetonate. *Annals of transplantation*, vol.9, no.1A (suppl.) 2004, 64-67.
14. Pamula E., Polok A., Menaszek E.: Degradable scaffold materials for cartilage regeneration. *Engineering of Biomaterials*, X, 69-72, 2007, 3-5.
15. Menaszek E., Pamula E.: The effect of pore size of resorbable PGLA foams on the tissue response. *In vivo study*. *Engineering of Biomaterials*, VIII, 47-53, (2005), 221-223.
16. Podrezov Yu., Firstov S., Szafran M., Kurzydłowski K.J.: Non-elastic behaviors of high-porosity ceramics and ceramic-polymer composites for medical applications. *Annals of transplantation*, vol.9, no.1A (suppl.) 2004, 15-19.
17. Paluch D., Pielka S., Solski L., Karas J., Jaegermann Z., Michalowski S.: The study of the cytotoxicity effects of the porous corundum implants containing antibiotics. *Engineering of Biomaterials*, VII, 37, 2004, 38-41.
18. Niedzielski K., Sindut R., Cholewa-Kowalska K., Laczka M., Kokoszka J.: New generation bioactive glass-ceramics as a substitute of bone – *in vivo* study. *Engineering of Biomaterials*, X, 67-68, (2007), 48-51.
19. Lewandowski R., Grzybowski J., Jaegermann Z., Polesinski Z.: The kinetic of antibiotic setting free from ceramic implants. *Polymers in Medicine*, 33,3, 2003, 3-11.
20. Szafran M., Bobryk E., Bereza M., Parzuchowski P.: Ceramic-polymer composites based on porous hydroxyapatite and lactide-carbonate macromonomers. *Engineering of Biomaterials*, VII, 38-42, (2004), 150-154.
21. Slosarczyk A., Paszkiewicz Z., Pitak A.: Rheological properties of hydroxyapatite slurries designer for preparation of highly porous bone implants



- using polyurethane foams as matrices. *Engineering of Biomaterials*, X, 61, (2007), 24-30.
22. Knowles J.C., Callut S., Georgiou G.: Characterisation of the rheological properties and zeta potential of a range of hydroxyapatite powders. *Biomaterials* 21, (2000), 1387-1392.
  23. Tadic D., Beckmann F., Schwarz K., Epple M.: A novel method to produce hydroxyapatite objects with interconnecting porosity that avoids sintering. *Biomaterials* 25, 2004.
  24. Chlopek J.: Composites in medicine. *Composites*, 1(1), (2001), 50-54.
  25. Ramakrishna S., Mayer J., Wintermantel E., Kam W. Leong: Biomedical applications of polymer-composite materials: a review. *Composites Sciences and Technology*, 61, (2001), 1189-1224.
  26. Szafran M., Rokicki G., Lipiec W., Konopna K., Kurzydowski K.: The porous ceramics with metals and polymers. *Composites*, 2 (25), (2002), 313-317.
  27. Yasuda H.Y., Mahara S., Umakoshi Y., Imazato S., Ebisu S.: Microstructure and mechanical property of synthesized hydroxyapatite prepared by colloidal process. *Biomaterials* 21, (2000), 2045-2049.
  28. Olah L., Borbas L.: Properties of calcium carbonate-containing composite scaffolds. *Acta of Bioengineering and Biomechanics*, vol.10, 1, 2008, 61-66
  29. Hench L.L.: Bioceramics: from concept to clinic. *Am. Ceram. Soc. Bull.*, vol. 72, nr 4, 1993, 93-98.
  30. Cao W., Hench L.L.: Bioactive materials. *Ceramics International*, 22, 1996, 493-507.
  31. de Groot K.: Hydroxylapatite as coating for implants. *Interceram*, 4, 1987, 38-41.
  32. Ratner B.D.: *Biomaterials Science. An introduction to materials in medicine*. Ed. Ratner B.D., Hoffman A.S., Schoen F.J., Lemons J.E. Academic Press, 1996.
  33. Biocybernetics and biomedical engineering 2000. Nalecz M. [red.], *Biomaterials*, PAN, EXIT, Warsaw, 2003.
  34. Bach Fr.W., Bormann D., Kucharski R., Wilk P.: Production and properties of foamed magnesium. *Cellular Metals and Polymers*. Eds. Springer, Zurich 2005, 77-80.
  35. Switzer E.: Resorbierbares metallisches osteosynthesematerial-untersuchungen zum resorptionsverhalten im meerschweinchenmodell. *Vet. Med. Diss.*, Hanover, 2005.
  36. Bach Fr.W., Kucharski R., Bormann D.: Magnesium compound structures for the treatment of bone defects. *Engineering of Biomaterials*, IX, 56-57, (2006), 58-61.
  37. Bach Fr.W., Kucharski R., Bormann D., Besdo D., Besdo S., Hackenbroigh Ch., Thorey Fr., Meyer-Lindenberg A.: Design of resorption properties of the metal bane implants-application in vivo. *Engineering of Biomaterials*, IX, 56-57, (2006), 54-58.

38. Gryn K., Chlopek J.: Hydroxyapatite scaffolds by “Robocasting” for medical applications-preliminary tests. *Engineering of Biomaterials*, XI, 76, 2008, 13-16.
39. Cesarano J., Clavert P.: Freeforming objects with low binder slurry. US Patent #6027326, 2000.
40. Saiz E., Gremillard L., Menendez G., Miranda P., Gryn K., Tomsia A.P.: Preparation of porous hydroxyapatite scaffolds. *Materials Science and Engineering, C*, 27, 2007, 546-550.
41. Miranda P., Saiz E., Gryn K., Tomsia A.P.: Sintering and robocasting of  $\beta$ -tricalcium phosphate scaffolds for orthopaedic applications. *Acta Biomaterialia*, 2, 2006, 457-466.
42. Li J.P., Habibovic P., Van del Doel M., Wilson C.E., de Wijn J.R., van Blitterswijk C.A., de Groot K.: Bone ingrowth in porous titanium implants produced by 3D fiber deposition. *Biomaterials* 28 (2007), 2810-2820.
43. Fang Z., Starly B., Sun W.: Computer-aided characterization for effective mechanical properties of porous tissue scaffolds. *Computer-Aided Design* 37 (2005), 65-72.
44. Chua Chee K., Leong Kah F.: *Rapid Prototyping; Principles & Applications in Manufacturing*. Willey & Sons 1997.
45. Lewis J.A.: Direct-write assembly for ceramics from colloidal inks. *Solid State & Materials Science* 6, (2002), 245-250.
46. Stuecker J.N., Cesarano J., Hirschfeld D.A.: Control of the viscous behaviour of highly concentrated mullite suspensions for robocasting. *Journal of Materials Processing Technology* 142, (2003), 318-325.
47. Kalita S.J., Bose S., Hosick H.L., Bandyopadhyay A.: Development of controlled polymer-ceramic composite scaffolds via fused deposition modeling. *Materials Science and Engineering, C* 23, (2003), 611-620.
48. Armistead R.A., Stanley J.H.: Computer tomography: A versatile technology. *Advanced Materials & Processes* 2/97, 33-36.
49. Uklejewski R., Winiecki M., Rogala P.: On the structural-adaptive compatibility of bone with porous coated implants on the base of traditional one-phase and the modern two-phase poroelastic biomechanical model of bone tissue. *Engineering of Biomaterials*, IX, 54-55, (2006), 1-13.