SIGNIFICANCE OF BIOCERAMICS FOR BONE SURGERY

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The paper presents ceramic implant materials used in orthopaedics, restorative dentistry, maxillofacial surgery and otholaryngology. In addition to oxide ceramics, also materials on the basis of calcium phosphates are presented, including composites with hydroxapatite or TCP matrix. Possible types of behaviour of implantation materials and living tissues as well as resulting classification of biomaterials, subdivided into: nearly inert, bioactive and resorbable, are discussed. Attention was drawn to the most prospective directions of research studies of biomaterials for the future.

Key words: bioceramics, implantation, bone substitution.

1. INTRODUCTION

Reconstructive medical activities, connected with filling the tissue defects, including bones, are brought about by the following factors:
- pathological changes, to which the human organism is subjected in the course of life,
- injuries connected with tissue defects,
- psychological, cosmetic and social considerations,
- optimisation of drug delivery systems.

The basic reconstructive material used for filling hard tissue defects was and continues to be natural bone. It is applied in the form of autogenic grafts and homogenous implants. In addition, use is made of materials obtained through the chemical or thermal treatment of animal bone, these being classified as either heterogeneous or xenogeneic preparations. Commonly used bone substitutes include the following alloplastic materials: metals and their alloys, bioglass, glassceramics, oxide bioceramics, calcium phosphate-based materials and composites.
2. INTERACTION AT THE IMPLANT-TISSUE INTERFACE

When designing and applying implants, it is necessary to keep in mind various possible reactions that may occur between the biomaterials from which the implant is made and the surrounding tissue [1]. If the material implanted into the organism is toxic, the surrounding tissue dies. If, however, the material is nontoxic and biologically inactive (nearly inert), a fibrous capsule of varying thickness forms around the implant. And if the implanted material is nontoxic and bioactive – a bonding between the tissue and the implant is observed. In the environment of a living organism, if the material is nontoxic and dissolves, the natural host tissue replaces it.

The mechanism of tissue attachment to the implant is directly related to the type of tissue response at the implant-tissue interface. The relative reactivity shown in Fig. 1 (case A) correlates very closely with the rate of formation of an interfacial bond of ceramic, glass, or glass-ceramic implants with bone. Fig. 1 (case B) presents time-dependence of formation of bone bonding at the implant – tissue interface.

![Graph showing bioactivity spectra for various bioceramic implants](image)

**Fig. 1.** Bioactivity spectra for various bioceramic implants [1]: (A) relative rate of bioreactivity, (B) time-dependance of formation of bone bonding at an implant interface.
When there are no open pores on the surface, materials described as "nearly inert" (e.g. dense alumina ceramics, dense Si₃N₄) do not bond chemically or fix biologically with the tissue. Fibrous tissue develops around such an implant, both from the direction of hard tissue and soft tissue, until finally it is surrounded by a sort of capsule. The thickness of the fibrous capsule differs depending on the type of material and the method of implant insertion, and may equal as much as a few hundred micrometers.

If the porous implant is made from a nearly inert material (e.g. porous Al₂O₃), then following implantation, there will occur the ingrowth of tissue into the surface pores or even throughout the implant. This leads to so-called biological fixation, which stabilises and strengthens the implant. Proper pore size is the precondition that must be fulfilled in order for the tissue penetrate and maintain its viability. It must equal at least 100 µm. However, a greater pore size, of 300–400 µm, is decidedly more advantageous.

Materials described as bioactive generate a specific biological response at the implant-tissue interface, as a result of which the implant connects directly with the tissues of the living organism, without the presence of a fibrous capsule. Nevertheless, parameters such as the time-dependence of bonding, the strength of bond, the mechanism of bonding and the thickness of the bonding zone vary for different bioactive materials. Bioactive materials are intermediate between resorbable and bioinert. They include bioactive glasses such as “Bioglass”, bioactive glass-ceramics such as “Ceravital”, A-W glass-ceramics or machinable glass-ceramics, dense HAp such as “Durapatite” or “Calcite", and bioactive composites such as HAp – polyethylene, HAp - Bioglass, and stainless steel fiber – reinforced bioglass.

Resorbable biomaterials are designed to degrade gradually over a period of time and be replaced by the natural host tissue. In the case of bone implants, they are the optimal solution, however on condition that the rate of resorption is fully synchronised with the rate of new tissue formation. In addition, during the period of degradation it is necessary to maintain the proper strength and stability of the biomaterial-tissue interface. Resorbable biomaterials include TCP (tricalcium phosphate) and resorbable polymers, such as poly(lactic acid) and poly(glycolic acid).

### 3. The significance of bioceramics

Among implantation materials used as substitutes for bone tissue, ceramic materials play a prominent role. Following implantation, these materials adapt well in living organisms, while upon contact with physiological factors they do not
undergo destruction (or only partially). They are non-irritable, non-carcinogenic, characterised by a considerable tolerance of sterilisation, and highly biocompatible with both hard and soft tissue. Bioceramics are made from elements which are either abundant in the physiological environment or do not constitute building materials of the organism, but are characterised by an extremely limited negative tissue reaction.

Table 1. Mechanical properties of cortical bone, cancellous bone, dentine and enamel.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Cortical bone</th>
<th>Cancellous bone</th>
<th>Dentine</th>
<th>Enamel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bending strength [MPa]</td>
<td>160&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>245 - 268&lt;sup&gt;b&lt;/sup&gt;</td>
<td>76&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>160 - 180&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>60 - 160&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>50 - 60&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10 - 70&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>124 - 174&lt;sup&gt;b&lt;/sup&gt;(p)</td>
<td></td>
<td>21 - 53&lt;sup&gt;b&lt;/sup&gt;</td>
<td>10&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>49&lt;sup&gt;b&lt;/sup&gt;(n)</td>
<td></td>
<td>51.7&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10.3&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Compressive strength [MPa]</td>
<td>170 - 193&lt;sup&gt;b&lt;/sup&gt;(p)</td>
<td>1.9 - 7.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>300 - 380&lt;sup&gt;a&lt;/sup&gt;</td>
<td>250-550&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>133&lt;sup&gt;b&lt;/sup&gt;(n)</td>
<td></td>
<td>250 - 350&lt;sup&gt;b&lt;/sup&gt;</td>
<td>95 - 370&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>295&lt;sup&gt;c&lt;/sup&gt;</td>
<td>384&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Shear strength [MPa]</td>
<td>54&lt;sup&gt;b&lt;/sup&gt;(p)</td>
<td>-</td>
<td>69 - 147&lt;sup&gt;b&lt;/sup&gt;</td>
<td>64 - 93&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Young modulus in bending [GPa]</td>
<td>3 - 30&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.18 - 0.33&lt;sup&gt;c&lt;/sup&gt;</td>
<td>15 - 20&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10 - 90&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>17 - 19&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>131&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>15.8&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td>18.2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>82.4&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fracture toughness K&lt;sub&gt;1c&lt;/sub&gt; [MPa . m&lt;sup&gt;1/2&lt;/sup&gt;]</td>
<td>2 - 12&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fracture surface energy [J . m&lt;sup&gt;-2&lt;/sup&gt;]</td>
<td>390 - 560&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>6000 (low strain rate)&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>98 (high strain rate)&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness (Knopp)</td>
<td>132 - 166&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>400 - 3500</td>
</tr>
</tbody>
</table>

p - parallel direction related to bone axis;  
N - normal direction related to bone axis;  
<sup>a</sup> [3]; <sup>b</sup> [6]; <sup>c</sup> [8].

The disadvantages inherent in the majority of ceramic implants are their brittleness and insufficient strength parameters. A comparison of the basic mechanical properties of the compact human bone, the cancellous bone and the teeth enamel with those of bioceramic materials (Table 1) shows that the latter fail to satisfy a number of relevant requirements.
Ceramic implants are used primarily to substitute hard tissue, that is bones and teeth, as dense or porous blocks, granules and powder, and also in the form of ceramic coatings on metal implants [2].

4. CEROSIUM

Viewed from a historical perspective, this material symbolises the first successfully concluded attempt at using ceramics for long bones replacement. This material, developed in 1963 by L. Smith, is a composite made from porous ceramics impregnated with epoxy resin. The ceramic matrix comprises anorthite (50 mass.%), Mg-Al spinel (20 mass.%), corundum (28 mass.%) and other minerals (2 mass.%). Its chemical analysis is as follows:

\[
\begin{align*}
\text{Al}_2\text{O}_3 & \quad 63.10 \text{ mass.}\% \\
\text{SiO}_2 & \quad 23.00 \text{ mass.}\% \\
\text{CaO} & \quad 6.90 \text{ mass.}\% \\
\text{MgO} & \quad 5.10 \text{ mass.}\% \\
\text{Na}_2\text{O} & \quad 0.60 \text{ mass.}\% \\
\text{K}_2\text{O} & \quad 0.60 \text{ mass.}\% \\
\text{Fe}_2\text{O}_3 & \quad 0.50 \text{ mass.}\% \\
\text{TiO}_2 & \quad 0.20 \text{ mass.}\% 
\end{align*}
\]

The epoxide fills 48% of the pores produced in the fired ceramic matrix.

By surface leaching of the ceramics, it is possible to obtain a material with a porous surface (pore size: 18 – 23 μm, pore depth: 50 – 70 μm). In terms of bending strength, CEROSIUM equals cancellous bone (~ 80 MPa). Equally similar are the Young's modulus values for both CEROSIUM and bone. However, information presented in the literature on the behaviour of this material in the environment of a living body differs. Extremely positive opinions alternate with reports describing failures in the application of CEROSIUM. These result from weak bone adhesion and the development of necrotic reactions under the influence of pressure applied. In practical applications, it has been observed that implants made from CEROSIUM are surrounded by a fibrous capsule, while 3 months after implantation their bending strength is reduced by 50%. Thus, the biomaterial in question has been withdrawn from common use [3].

5. ALUMINA CERAMICS

At present, alumina is the oldest ceramic material commonly used in medicine. Although as early as 1932 Max Rock patented the idea of using alu-
mina as a biomaterial, it was only in the seventies that research into \( \alpha \text{Al}_2\text{O}_3 \) (corundum) began in earnest and the material was introduced to implantation. In accordance with ISO 6474 Standard (Table 2), \( \text{Al}_2\text{O}_3 \) powders used for manufacturing implants and the implantation materials made therefrom have to meet a number of requirements.

**Table 2. Implants for surgery – Ceramic materials based on alumina (ISO 6474–1981 (E)) [4].**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina content [wt %]</td>
<td>( \geq 99.5 )</td>
</tr>
<tr>
<td>Density [g/cm(^3)]</td>
<td>( \geq 3.9 )</td>
</tr>
<tr>
<td>Average grain size [( \mu \text{m} )]</td>
<td>( &lt; 7 )</td>
</tr>
<tr>
<td>Microhardness [HV]</td>
<td>( \approx 2300 )</td>
</tr>
<tr>
<td>Compressive strength [MPa]</td>
<td>( \approx 4000 )</td>
</tr>
<tr>
<td>Bending strength [MPa]</td>
<td>( \geq 400 )</td>
</tr>
<tr>
<td>Young modulus in bending [GPa]</td>
<td>380</td>
</tr>
<tr>
<td>Impact strength [J/m(^2)]</td>
<td>( \geq 4000 )</td>
</tr>
<tr>
<td>Wear resistance [mm(^3)/h]</td>
<td>( \leq 0.01 )</td>
</tr>
<tr>
<td>Corrosion resistance [mg/m(^2) . day]</td>
<td>( \leq 0.1 )</td>
</tr>
</tbody>
</table>

The advantages of alumina ceramics are good biocompatibility, inertness and good mechanical properties. In the case of dense \( \alpha \text{Al}_2\text{O}_3 \) sinters, the parameters of which exceed the ISO Standard requirements, it is possible to achieve even very good results in terms of fatigue strength, impact resistance and ultimate compressive strength. A chemical purity of biocorundum in excess of 99.8 mass.% and an average grain size lower than 4 \( \mu \text{m} \) are required. One should underline the excellent tribological properties and good machinability of alumina ceramics, which make it possible to obtain very smooth surfaces. Thus, corundum is used for manufacturing the heads – and sometimes also the sockets – of hip joint endoprostheses.

The disadvantages of alumina implants are brittleness (\( K_{ic} = 5–6 \) MPa.m\(^{1/2}\)), a decline in strength parameters under “in vivo” conditions, and the fact that, if released from implants, Al may negatively influence the human nervous system.
Apart from applications connected with the manufacture of artificial hip joints, alumina ceramics are used for filling bone defects in spinal surgery, maxillofacial surgery, otolaryngology, and orthopaedics [1, 4].

6. ZrO₂ Ceramics (Zirconia)

ZrO₂ ceramics, especially those manufactured on the basis of partially stabilized ZrO₂, are characterised by very good mechanical properties, which are attributed to the phase transition strengthening mechanism unique to these materials. Tetragonal ZrO₂ polycrystals (TZP) stabilised among others with yttrium oxide (Y-TZP) are characterised by the following:

- high abrasion resistance;
- bending strength of 1–1.5 GPa;
- fracture toughness 8–10 MPa.m¹/²;
- Young’s modulus ~200 GPa.

While biocompatibility of zirconia is comparable with that of alumina, TZP are typified by a considerably greater mechanical strength, which makes it possible to advantageously reduce the diameter of heads of hip joint endoprostheses from 32 mm to 22 mm. Stabilized zirconia can be used for load bearing applications. Femoral heads made of ZrO₂ were introduced about 10 years ago in France, USA and Australia. It has been shown that the wear rates, when zirconia heads are articulating against polyethylene cups, are 5 to 10 times lower than that of the pairing stainless steel-polyethylene, and approximately 50% lower than that of the pair Al₂O₃-polyethylene. However, the value of this parameter is considerably greater when a zirconia head is paired with a ceramic (e.g. Al₂O₃) socket.

In professional literature there have appeared reports to the effect that ZrO₂ ceramics age in the environment of a living organism and that as a result, their strength parameters deteriorate with the passage of time [1, 3, 5].

7. TiO₂ Ceramics (Titania)

To date, this material has been used solely as a plasma coating of other materials. From the three polymorphic modifications of TiO₂, rutile is the most promising phase for medical applications.
8. Carbides and nitrides

Carbides and nitrides have aroused considerable interest as potential implantation materials. Research has focused on compounds such as Si$_3$N$_4$, TiN, TaN, HfN, ZrN, TiC$_x$, and TaC$_x$. Carbides that are researched in order to establish whether they are suitable for medical applications, are non-stoichiometric compounds ($x \leq 1$) with extremely high melting points, even in excess of 4000 °C. From among the compounds belonging to this group, the greatest hopes rest with silicon nitride – Si$_3$N$_4$.

Due to the fact that the procedure required for obtaining materials based on carbides and nitrides is complicated, and thereby costly, the scope of their possible medical applications is limited [3].

9. Bioceramics based on calcium phosphates

Materials containing calcium phosphates, and in particular hydroxyapatite (HAp) and whitlockite ($\beta$TCP), are prominent amongst ceramic implantation materials.

Hydroxyapatite bioceramics, due to their chemical and mineralogical similarity to the inorganic phases of bone and teeth, do not show any cytotoxic effects following implantation. Furthermore, they are characterised by excellent biocompatibility with both hard and soft tissues. Due to their bioactivity, hydroxyapatite implants may bond directly with the bone. The hydroxyapatite ceramics reveal good osseocompatibility. Unfortunately, due to unsatisfactory mechanical properties and low reliability, HAp implants cannot be used in places which carry considerable mechanical load.

Initial HAp powders used for manufacturing hydroxyapatite implants are prepared by means of the wet methods and solid state reactions. The wet methods can be divided into three groups: precipitation, hydrothermal technique, and hydrolysis of other calcium phosphates. Hydroxyapatite of a high purity can be obtained by applying the sol-gel technique.

The characteristics of initial powders, and in particular their Ca/P molar ratio, exert a considerable influence on the phase composition and physico-chemical properties of implantation materials made therefrom. It has been shown that it is possible to obtain a monophase hydroxyapatite material in which hydroxyapatite, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, constitutes the only crystalline phase, when using powders in which the Ca/P molar ratio equals 1.67, thus corresponding to stoichiometric hydroxyapatite. If the Ca/P molar ratio exceeds the value of 1.67, CaO forms during sintering. This brings about a considerable reduction of the mechanical
strength of implants. In extreme situations, when contact is made with moisture, the increase in volume which accompanies the formation of Ca(OH)$_2$ may lead to the complete decohesion of the implant. If, in turn, the Ca/P molar ratio of the initial hydroxyapatite powder is less than 1.67, then during sintering $\beta$ and/or $\alpha$TCP are generated. The presence of TCP increases the biodegradation of implants. It may also negatively influence the densification of the material during sintering and lead to the slow development of cracks and fractures [2, 6 – 11].

9.1. Dense hydroxyapatite ceramics

Most often, dense HAp implants are formed by uniaxial pressing, slip casting, injection moulding, cold isostatic pressing (CIP) or hot isostatic pressing (HIP). The process of sintering is carried out under temperatures ranging from 1150 °C to 1300 °C. It has to be taken into account that higher sintering temperatures may lead to the growth of grains and/or the decomposition of HAp, which factors could lead to the strength degradation.

Techniques such as hot isostatic pressing (HIP), hot pressing (HP), and post-sintering make it possible to reduce the temperature of the densification process, decrease the grain size and obtain higher densities. In addition, they ensure a better stability of HAp and result in a more advantageous microstructure of the material, which in effect serves to improve the mechanical parameters of implants. Table 3 shows the mechanical properties of dense hydroxyapatite bioceramics. The considerable scatter of results is brought about by the following factors: the statistical character of strength distribution, the presence of remaining porosity, the different sizes of grains in the material following sintering, and the presence of impurities.

Low $K_{ic}$ and Weibull's modulus values, as well as a considerable susceptibility to the gradual development of cracks (especially in the presence of humidity) are indicative of the low reliability of hydroxyapatite implants [12 – 14].

9.2. Porous hydroxyapatite ceramics

So far, of all the biomaterials based on calcium phosphates, porous hydroxyapatite ceramics are the most widely applied in medicine. This material is used in the form of porous blocks and porous granules of various sizes. The considerably lower (with relation to dense sinters) strength parameters of implants made from porous HAp are recompensed by their better stability in bone defects. When the living tissue grows into the pores of the material, it ensures a good attachment to the bone. This biological fixation is additionally strengthened as a result of the creation, due to the bioactivity of hydroxyapatite, of a chemical bond at the
implant-bone interface. The minimum pore size that enables the tissue to ingrow and maintain itself in the pores is 100 µm.

Table 3. Mechanical properties of dense HA\(\text{P}\) bioceramics.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Dense HA(\text{P}) material</th>
<th>Porous HA(\text{P}) material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bending strength [MPa]</td>
<td>40 – 300(^{a)})</td>
<td>2 – 11(^{b)})</td>
</tr>
<tr>
<td></td>
<td>38 – 250(^{b)})</td>
<td></td>
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<tr>
<td></td>
<td>113 – 196(^{c)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 – 1000(^{b)})*</td>
<td></td>
</tr>
<tr>
<td>Compressive strength [MPa]</td>
<td>300 – 900(^{a)})</td>
<td>2 – 100(^{b)})</td>
</tr>
<tr>
<td></td>
<td>120 – 900(^{b)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>308 – 509(^{g)})</td>
<td></td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>40 – 300(^{a)})</td>
<td>3(^{b)})</td>
</tr>
<tr>
<td></td>
<td>38 – 300(^{b)})</td>
<td></td>
</tr>
<tr>
<td>Torsional strength [MPa]</td>
<td>50 – 76(^{g)})</td>
<td>–</td>
</tr>
<tr>
<td>Fracture toughness K(_{\text{IC}}) [MPa (\text{m}^{1/2})]</td>
<td>0.6 – 1.0(^{a)})</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.8 – 1.2(^{b)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.69 – 1.16(^{c)})</td>
<td></td>
</tr>
<tr>
<td>Fracture surface energy [J (\text{m}^{-2})]</td>
<td>2.3 – 20(^{a)})</td>
<td>–</td>
</tr>
<tr>
<td>Young modulus [GPa]</td>
<td>80 – 120(^{a)})</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>35 – 120(^{b)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.5 – 112(^{c)})</td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vickers [GPa]</td>
<td>3.0 – 7.0(^{b)})</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>5.2 – 6.5(^{d)})</td>
<td></td>
</tr>
<tr>
<td>Knapp [GPa]</td>
<td>4.8 – 4.9(^{e)})</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>(~ 2.0(^{f)})</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a)}\) [3]; \(^{b)}\) [6]; \(^{c)}\) [7]; \(^{d)}\) [9]; \(^{e)}\) [10]; \(^{f)}\) [11]; \(^{g)}\) [8];
\(\ast\) HA\(\text{P}\) single crystals

The classical method of manufacturing porous hydroxyapatite ceramics consists in sintering the HA\(\text{P}\) powder with appropriate pore-creating additives (paraffin, naphthalene, hydrogen peroxide). Porous HA\(\text{P}\) implants are also fabricated on the basis of polyurethane sponge [16, 17].

Porous hydroxyapatite ceramics undergo extremely slow biodegradation (totalling a few % per year) and are only gradually replaced by bone. In fact, this process is so slow that for a number of years it was considered that HA\(\text{P}\) ceramics are non-resorbable [8, 18].
9.3. Hydroxyapatite coatings

The biocompatibility of metal implants and implants produced from inert ceramics can be considerably increased through the application thereto of a thin hydroxyapatite layer. Such biomaterials bring together high mechanical strength with a very good biological compatibility with the living tissues.

The main method of applying hydroxyapatite layers is the plasma technique. The phase and chemical composition, microstructure, crystallinity and implant surface adhesive force are influenced by the selection of parameters of the sputtering process itself (plasma gas composition, rate of gas flow, distance between the burner mouth and the place where the coated specimen is located).

Hydroxyapatite coatings may also be applied to metals and ceramics using other methods, such as electrophoresis, CVD and PVD techniques, thermal decomposition, ion sputtering, or electrochemical deposition [20, 21].

Although the durability of HAp coatings varies, the majority of results published hitherto confirms the advantageous influence thereof on the behaviour of implants in the environment of a living organism. The coating of hip joint endoprostheses and knee joint endoprostheses with hydroxyapatite has made it possible to introduce so-called cement-free endoprostheses to surgery. There is clinical proof that HAp coatings improve the osseointegration of femoral and knee joints, and also of dental implants. Up to now, coating seems to be the most important and promising application of hydroxyapatite in medicine [8, 22].

9.4. Whitlockite ceramics (TCP)

Despite the fact that whitlockite ceramics (TCP) – $\beta$(Ca$_3$(PO$_4$)$_2$ – equal hydroxyapatite ceramics in terms of biocompatibility, they are used considerably less frequently. TCP, due to a susceptibility to resorption and biodegradation higher than HAp, does not always bond strongly with bone. If the resorption of the biomaterial proceeds at a greater rate than the formation of a new bone, such fixation will not occur [2, 23].

9.5. Biphase hydroxyapatite – whitlockite ceramics

Over the last dozen or so years, opinions regarding TCP and the presence of TCP as a secondary phase in hydroxyapatite ceramics have undergone a change. Earlier reports warned against its presence, as a highly undesirable admixture of hydroxyapatite implants. It was feared that the compound would negatively influence the mechanical properties of implantation materials, this for the following reasons:
- the polymorphous transition of $\beta$TCP into $\alpha$TCP and the accompanying change in volume of 7.3%;
- differences existing between coefficients of thermal expansion of coexistent phases;
- the susceptibility of whitlockite material to swelling under the influence of moisture.

The above-mentioned phenomena were regarded as the potential causes of the so-called ageing of biomaterials containing TCP, which in extreme cases could lead even to the complete desintegration of implants manufactured therefrom.

Subsequent research has shown that biphasic HA-pTCP ceramics constitute an interesting implantation material, with a controllable degree and rate of resorption. When the HA-pTCP ratio is appropriate, the mechanical strength and fracture toughness exceed those of monophase HA-p ceramics [2, 24].

9.6. HA-p and TCP-based composites

Composites are materials that are obtained by intentionally combining two or more natural or synthetic materials with the objective of creating a new multiphase system, the properties of which exceed those of each constituent material taken separately. Normally, the discontinuous phase of composites is stronger and harder, being defined as the strengthening phase, while the continuous phase – i.e. the matrix – is weaker.

For medical purposes, composite materials based on calcium phosphates are created with the objective of obtaining biomaterials with a better mechanical properties than hydroxyapatite and whitlockite ceramics, a higher $K_{IC}$ value, and a lower Young's modulus value. These materials bring together the high biocompatibility and bioactivity of the HA-p or TCP matrix with a good mechanical strength conditioned by the strengthening phase. In the case of these composites, ceramics, bio-glass, carbon, metals or polymers may be used as the strengthening phase [2, 6, 25 – 28]. In recent years many reinforcements, including particles, nanoparticles, platelets, long fibres, whiskers and metal dispersoids, have been used in hydroxyapatite and whitlockite ceramics to improve their reliability. The following composites have been and continue to be the subject of intensive research:

HA-p – TCP,
HA-p – particles: Al$_2$O$_3$, (3Y) ZrO$_2$,
HA-p – whiskers: SiC, Si$_3$N$_4$ diopside,
HA-p – long metal fibres: FeCralloy,
HA-p – fibres: ZrO$_2$, Al$_2$O$_3$, C,
HA-p – nanoparticles or platelets SiC,
HAp – polyethylene,
HAp – collagen,
HAp – bioactive glass,
HAp – HAp whiskers,
HAp – coated titanium alloy.

The properties of composites are dependent on the characteristics of their constituent materials, their distribution and mutual orientation, and also on interaction between them.

To date, composites with an HAp matrix have not found wide application in medicine. This may result from the fact that, compared with a pure hydroxyapatite, their biocompatibility and bioactivity are lower. In addition, research has shown that the presence of another phase facilitates the decomposition of HAp to TCP, while the evaporation of water which accompanies this process may negatively influence the sintering. Furthermore, in the case of composites containing whiskers there always exists the possibility that the progressive biodegradation of the material may lead to the release of whiskers into the surrounding tissue, which could result in major health problems.

Composite materials frequently require complicated techniques of obtainment, such as hot pressing (HP) or hot isostatic pressing (HIP); this factor considerably increases overall costs and may undoubtedly influence their range of applications. For the future, the most promising hard tissue replacement implants appear to be HAp-collagen, fibrous HAp-reinforced polymers, and fibres whiskers reinforced HAp.

9.7. Application of bioceramics based on calcium phosphates

Calcium phosphate ceramics are used in preventive and restorative dentistry, orthopaedics, otolaryngology, and in maxillofacial surgery [2].

To date, hydroxyapatite bioceramics are the most widely applied from among this group of materials. The range of applications of this implantation material, either synthetic or obtained on the basis of natural coral, includes the following:
- coatings for orthopaedic and dental metal implants,
- orbital implants for orbital floor fractures,
- fillers for the repair of periodontal defects or bone loss,
- porous grafts for immediate tooth-root replacement after extraction to prevent alveolar ridge resorption,
- ear implants,
- repair of maxillofacial defects,
- direct and indirect pulp-capping materials,
- treatment of enamel hypoplasia,
- inhibition of pathologic teeth abrasion,
- drug delivery systems,
- dentifrices: toothpastes and toothpowders,
- dental cements,
- treatment of dentine hypersensitivity.

10. PERSPECTIVES IN BIOMATERIALS SCIENCE

The field of biomaterials is relatively young, with perhaps 40 years of formal history. It is a typically interdisciplinary field, in which the joint efforts of engineers, biologists and doctors bear fruit in the elaboration and medical implementation of ever newer and better implantation materials [1].

Lately, considerable attention was focused – both in discussions and the literature – on the search for a new generation of biomaterials, suited to the requirements of the 21st century, that could be used for substituting the tissue and organs of living organisms.

Ever more frequently, the old empirical research-based style, hitherto commonly applied in biomaterials science, is being replaced by a newer operating method which makes use of the information technology. Now we have the possibility of designing materials and optimising their properties on the computer screen.

Undoubtedly, composite materials - including nanocomposites - will in future play an ever more prominent role in the production of implants. Composite materials combine the desired mechanical properties of each of the two phases in one materials system. It is presumed that research will now tend to focus on biomimetic materials, which imitate the construction, composition and natural properties of works of nature.

The concept of biocompatibility will need to be clarified in detail, in particular at the molecular level. There is mounting evidence that it is closely associated with cellular activation and linked to chemical communication between cells.

In the field of biomaterials, the greatest hopes for the future rest with intelligent materials and artificial hybrid organs. The latter constitute specific composite systems made up of living cells or tissue and synthetic biomaterials.

The majority of bioreactions occur at interfaces, yet the formal study of interfaces is just developing in biomaterials. Due to the fact that the nature of cellular reactions to materials is largely dependent on the microstructure – and in particular on the porosity – of the specific material, it is highly probable that in future research will also be devoted to issues concerned with so-called implantation material architecture.
The future of research in the field of biomaterials lies in biomaterials with built-in synthetic or natural receptors, which are characterised by a capacity for specific interactions with biological systems.

Research into the obtainment of implantation materials by applying new techniques must be considered to be equally promising. One of these is the sol-gel method, which makes it possible to produce bioceramic materials with a high purity under low temperatures.

The next few years will show us in which direction biomaterials engineering will progress and what new implantological opportunities will appear as a result.

REFERENCES


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