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GLASS AND GLASS-CERAMIC POROUS MATERIALS FOR BIOMEDICAL APPLICATIONS

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Abstract: Biosilicate glasses and glass-ceramic materials obtained on their basis are an important research area in tissue engineering due to their ability to regenerate bones. The most important features of bioactive glasses include: the ability to biodegrade and high bioactivity. Appropriate porosity, pore size, surface structure and topography, chemical composition and ion release kinetics, as well as mechanical properties enable the adhesion of mesenchymal cells and their differentiation towards osteoblast cells and stimulate further proliferation and angiogenesis. This study concerns the subject of bioglass, in particular Bioglass 45S5 and glass-crystalline porous materials in the context of their properties enabling the reconstruction of bone tissue and possible applications. The article addresses crucial issues of shaping the properties of glass and glass-crystalline porous structures by introducing changes in their composition and the method of their production, and also discusses the importance of foaming agents.

Keywords: bioglass, glass-ceramic materials, porosity, foaming agents, bioactivity,

1. INTRODUCTION

In 1969, Professor Larry L. Hench proposed a glass composition that showed exceptional biocompatibility and the ability to bond with rat bone, and the biodegradation of its surface occurred within 10 to 30 days. The glass composition consisted of 45% $SiO2$, 24.5% $Na2O$, 24.4% CaO and 6% $P2O5$ (wt%) and became the basis for further development of glass bioactive materials (Cannio et al., 2021). Bioglasses are designed by selecting their chemical composition, taking into account the manufacturing conditions, so as to guarantee high structural compatibility with living tissue and meet the requirements necessary for their application (Yang et al., 2001).

Biomaterials, besides their purely technical role (Opydo et al., 2019), also serve a significant societal function (Kuzior and Zozul'ak, 2019) due to their medical applications. An important issue in their case is the risk of corrosion and biocorrosion (Scendo et al., 2012; Scenco et al., 2013), which may require the use of various special coatings (Radek et al., 2019) and sophisticated quality techniques (Borkowski et al., 2012; Ulewicz, 2018). The use of Design of Experiments (DOE) methods is inevitable both in biomaterial research and their production processes (Pietraszek et al., 2020), along with appropriate training for involved technicians (Radek et al., 2023).

2. PROPERTIES AND APPLICATIONS OF BIOACTIVE GLASSES

Bioactive glasses consist of four basic components: silicon oxide (SiO_2), sodium oxide (Na_2O), calcium oxide (CaO) and phosphorus (V) oxide (P_2O_5). The network of bioactive glasses is composed mainly of silica. The source of silica may be alkoxysilanes, tetraethyl or tetramethyl orthosilicates and rice husk (90% silicon and 10% lignin), which constitutes 23% of the rice mass (Pereira et al., 2021). A novel and alternative source is biosilica from diatom cultures (Adams et al., 2017). The molecular structure of the glass is strongly disturbed, which is due to the presence of Na^+ and Ca^{2+} ions, which introduce non-bridged oxygen bonds; their presence makes bioactive glasses soluble in aqueous environments. Phosphorus introduced into the glass structure in the form of phosphorus (V) oxide is bound to Na^+ or Ca^{2+} ions into monophosphate or diphosphate complexes and does not bind to silicon (Cannio et al., 2021).

Bioactivity (bioreactivity) refers to materials that are capable of forming a permanent connection with tissue in the presence of body fluids. The silica content below 60%, an increase in the content of modifying oxides (>10% CaO) and a high CaO/P_2O_5 content ratio result in an increase in bioactivity, and the chemical composition determines the rate of glass biodegradation. Bioactivity is also increased by phosphates, which nucleate the crystallization of carbonate hydroxyapatite (HCA). The coordination number of silica determines the solubility of glass because it determines the number of bridge bonds per silicon atom, thus describing the network connectivity (Dziadek et al., 2015; Cannio et al., 2021). By modifying the oxide content in the composition of bioglass, materials with specific reactivity are obtained (Dziadek et al., 2015). Bioactivity is reduced after the introduction of multivalent ions that stabilize the glass structure, in the amount of 1.5 to 3% of oxides such as: Al_2O_3, B_2O_3, TaO_5, ZrO_2 (Adams et al., 2017). For bioactive glasses, a bioactivity index is determined, which informs about the time after which 50% of the material surface will be permanently bound to the tissue (Hench, 2006). The degree of bioactivity (IB) divides ceramic materials into osteoinductive (class A) and osteoconductive (class B). Bioglasses have a high bioactivity index (IB > 8) and belong to class A, their surface enables the settlement and colonization of stem cells, activates and stimulates proliferation and their differentiation towards osteoblasts. These materials bind on the surface to bone tissue and soft tissues (Dziadek et al., 2015) using two surface fixation mechanisms. Initially, a chemical connection takes place, therefore HCA is formed on the surface of the biomaterial to fuse the bioglass with the bone tissue. Then, biological connection occurs, which involves attaching collagen fibers to the surface of the biomaterial using electrostatic interactions, hydrogen or ionic bonds, which is used to create permanent connections with soft tissues (Cannio et al., 2021).

The kinetics of bioglass biodegradation and HCA formation are assessed in in vitro tests after immersing the glass in an aqueous phosphate solution imitating physiological fluids (SBF) at a temperature close to the human body temperature (37°C) (Borden et al., 2022). Cytotoxicity tests are conducted after glass implantation, based on the analysis of the chemical composition of physiological fluids or tissue fragments of organs in which elements released from the bioglass structure may have accumulated (Gerhard et al., 2010). In in vitro studies, 45S5 bioglass showed a beneficial effect on the expression of the vascular endothelial growth factor gene, increasing its secretion (Borden et al., 2022).

45S5 bioglass tends to crystallize during sintering and has poor mechanical properties (Erasmus et al., 2017). Currently, two bioglasses based on 45S5 Bioglass® are available on the market, differing in particle fraction (Cannio et al., 2021; Adams et al., 2017):

- PerioGlas® - NovaBone – 90-170 μm
- BioGran® - BIOMET2i™ – 300-355 μm

BioGrain® bioglass particles are combined with autogenous bone, and PerioGlas® bioglass particles are used alone in dentistry. A small amount of autogenous bone provides cells that maintain a normal immunohistochemical response, normal vascular development, and osteoblastic activity during bone repair (Cannio et al., 2021). Bioactive glasses have a unique set of properties, therefore they have great potential in biomedical applications as (Kaur et al., 2014):

- Material for implants and dental implants used in periodontal diseases, in endodontics they replace tooth root embryos and as gels for grading mineralization.
- Remineralizing material for dental hypersensitivity (Zhang et al., 2021).
- An antibacterial agent that uses released ions and the alkaline nature of bioglass to reduce the viability of bacteria in osteomyelitis in patients with diabetic foot (Giglio et al., 2020).
- Drug delivery medium for bone and marrow inflammation (Mazzoni et al., 2021).
- Material for the regeneration of soft tissue damage, including repair (Mazzoni et al., 2021): myocardial tissues - cardiac patch strategy; lung tissues – colonization of bioglass scaffolds; nervous tissue – NGC (Nerve Guidance Channel) method; skin and squamous epithelia - nanofibrous bioglass dressings and ointments with bioglass particles with antibacterial properties; stomach and duodenum epithelium - alkaline ions neutralize the action of stomach acids;

2.1 Doping and substitution of bioglass

Elements introduced as additions to the main composition of bioglass or as partial or even complete replacement of the main components allow the production of bioglasses with varying degrees of bioactivity and biodegradability. The release of trace elements must be strictly controlled so that the toxicity threshold is not exceeded Classic, well-known and little-known ions used for the production of bioglasses are marked on the periodic table - Fig. 1. (Pantulap et al., 2022).

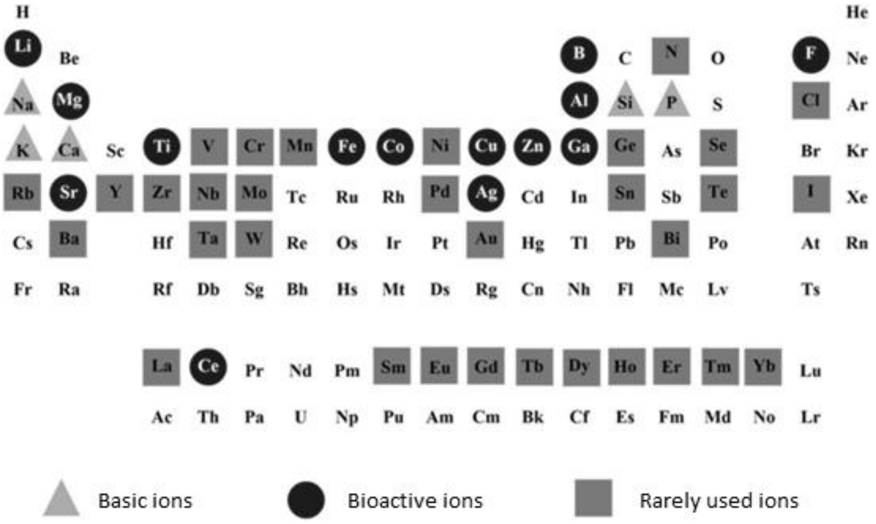

Fig. 1. Chemical elements used in the production of bioglass

Each of the trace elements and doped ions has its own role in the body, and each of the oxides introduced into the bioglass composition affects their properties. Less known ions play a major role in directing stem cell differentiation (Wetzer et al., 2020). The ions whose bioactivity has been confirmed include: Cl^-, Cr^{6+}, Ho^{3+}, Ba^{2+}, V^{5+}, Mn^{2+}, Bi^{3+}, Sm^{3+}, Se^{4+}, Sr^{2+}, Ta^{5+}, Y^{3+}, Tb^{4+}, Zr^{4+}, Ge^{2+}, Rb^+, Nb^{5+}, Er^{3+}, Te^{4+}, Au^{3+} (Pantulap et al., 2022).

2.2 Porous bioglass in tissue engineering

In tissue engineering, porous bioactive glasses are a substrate on which adhesion, enzymatic activation, proliferation and differentiation of cells occur, i.e. the transformation of stem cells into cells with specific functions and the formation of vascularized, healthy bone along with the degradation of the scaffold Bone marrow cells are autologous to the cells of damaged bone and can be stimulated with ions, proteins and growth factors (Yang et al., 2001).

The requirements for scaffolds mainly concern biomechanical properties, which must match the properties of the surrounding tissue. The scaffold should not cause any adverse reactions from the host organism. A suitable material should initially maintain its properties, allowing cells to initiate regeneration, and then gradually biodegrade. Finally, the scaffold should be completely replaced by new tissue (Yang et al., 2001). Correct spatial organization supports regeneration, a large surface promotes cell attachment and growth, and a large pore volume is intended to accommodate and transport cells. It is assumed that the proper size of a pore is its smallest dimension and is defined as diameter (Espinal, 2012). The best bone ingrowth occurs in materials with pore sizes ranging from 100 to 500 μm. It is assumed that a pore size greater than 100 μm and an open porosity greater than 50% are the absolute minimum enabling cell ingrowth and proper functioning of the scaffolds (Fu et al., 2011). For vascularization, pores of 5 μm are sufficient, fibroblasts or hepatocytes require pores of 5-20 μm, for skin regeneration it is 20-125 μm, and for fibrous tissue 500 μm or more. Connective porosity is important for cell transport and migration, shape determines adhesion strength, and pore tortuosity contributes to the rounded cell morphology. Too high open porosity and pore size may adversely affect the mechanical strength of scaffolds (Yang et al., 2001). The surface of the bioglass should be rough so that cells can stick to it, wettability affects cell adhesion and protein absorption, and porosity is the most important parameter describing the scaffold because it determines the extent to which the material will be useful in tissue engineering (Mabrouk, 2015). Glassy porous materials are characterized by compressive strength ranging from 0.2 to 150 MPa for porosities ranging from 30 to 95%. Another feature characterizing porous glass structures is their brittleness, which can be quantified by examining fracture toughness, Weibull modulus or work of fracture (Fu et al., 2011).

One of the most interesting applications of bioglass scaffolds is implantable drug delivery systems (Mazzoni et al., 2021). The drug delivery material should be bioinert or biodegradable, biocompatible, mechanically resistant and comfortable for the patient, and should carry the appropriate dose of drugs without the risk of release in an inappropriate place. The material should also be easily removed, manufactured and sterilized. So far, drug delivery systems based on bioglasses containing ions such as Dy^{3+}, Sm^{3+}, Eu^{3+}, N^{3-}, Rb^+, Se^{4+}, Mo^{6+}, Ni^{2+}, W^{6+} have been successfully used (Pantulap et al., 2022). The main areas of application are infections of the musculoskeletal system and cancer therapy, in which drug release occurs only in the presence of enzymes associated with the expression of cancer cells (Mazzoni et al., 2021).

3. BIOACTIVITY AND PROPERTIES OF GLASS-CERAMIC BIOMATERIALS

Glass-crystalline materials are obtained in the process of controlled crystallization of primary glasses or during the production or sintering of bioactive glasses. The formation of crystalline phases is influenced by particle size and the CaO/SiO2 ratio (Dávalos et al., 2020). Glass-crystalline materials based on bioglasses belong to bioactivity class A, showing high biological reactivity and have very good mechanical properties, exceeding the parent glass in terms of hardness, bending strength and crack resistance (El-Wassefy et al., 2021). When the glass-ceramic material is immersed in the SBF solution, three processes occur successively: leaching (a), dissolution (b) and precipitation (c) – Fig. 2. (Montazerian and Zanotto, 2016).

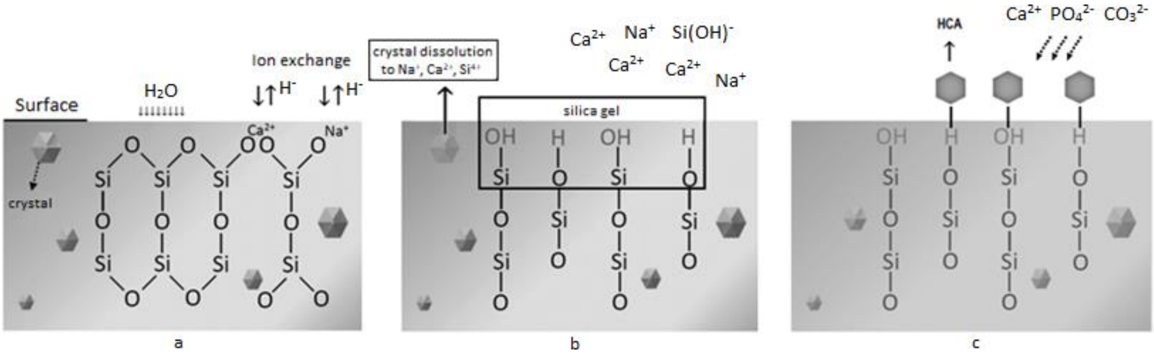

Fig. 2. Diagram of reactions occurring on the surface of glass ceramics in SBF solution

Leaching (a) is the release of alkalis such as Na^+, Ca^{2+} as a result of exchange with H^+. In the case of the amorphous phase, the release of modifying ions is rapid and the exchange leads to an increase in pH to values greater than 7.4. Dissolution (b) of the network occurs by breaking the –Si–O–Si–O–Si– bond by hydroxyl ions (OH^-). The integrity of the network is locally interrupted and silica is released into the solution in the form of silicic acid $Si(OH)_4$. The dissolution of crystalline phases embedded in the residual glass leads to the release of alkaline ions or alkaline earth element ions. Hydrated silica undergoes polycondensation on the surface and forms a layer of silica gel. During precipitation (c), Ca^{2+} and PO_4^{2-} ions that were released from the glass ceramics and present in the surrounding solution migrate to the surface, forming calcium phosphate (CaP). CaP is initially amorphous and then crystallizes to HCA by adding carbonate anions from the solution.

Studies using SBF show that crystalline phases do not negatively affect the formation of HCA, moreover, an appropriately selected composition of crystalline phases can improve the kinetics of HCA formation (Kokubo and Takadama, 2006). The crystallization process is responsible for increasing the strength of glass-crystalline materials. The high content of the crystalline phase results in overlapping of the microstructure and, as a result, an increase in bending strength. A similar effect is achieved by the elongated shape of the crystals. The increase in the volume of the crystalline phase and the size of the crystals increases the mechanical strength of glass ceramics, and ceramics with homogeneous crystals are more mechanically durable (Serbena et al., 2015). A similar effect is achieved by the elongated shape of the crystals. The large size of the crystals increases the mechanical strength of glass ceramics, and ceramics with homogeneous crystals are more mechanically durable (Serbena et al., 2015). The presence of pores negatively affects the mechanical properties if their shape is other than spherical. However, closed porosity and glass transition of the sample result in a significant increase in mechanical properties (Gerhardt and Boccaccini, 2010).

The basis for the classification of bioactive glass ceramics is the type of crystalline phases present in them and the resulting applications. The most known and commercially available glass-crystalline materials on the medical market include (Daskalakis et al., 2021): apatite materials for prosthetic phalanges, apatite-wollastonite (A+W) materials for endoprostheses coatings, apatite materials with mica for ear implants and orthopedic implants, apatite-free ceramics for disc-shaped implants, orbital implants, middle ear ossicles implants, and powders and coatings in dentistry. Other glass-ceramic materials that are currently used: apatite-mullite, kanansite-apatite, rananite, calcium-pyrophosphate, k-fluorichterite and alkali-free (Montazerian and Zanotto, 2016).

4. FOAMING AGENTS IN THE PRODUCTION OF POROUS GLASS CERAMICS

The production of porous glass ceramics includes phase separation, leaching process, sol-gel method, sintering and foaming (Montazerian and Zanotto, 2016). Sintering is a process of binding, molding or recrystallizing a powder moulder, which results in obtaining a more durable monolith. The use of foaming agents, due to their simplicity, is the most common method of producing glass-ceramic foams and involves mixing glass powder with a foaming agent. Foaming is the result of decomposition reactions, e.g. due to the release of carbonates and sulphates or oxidation reactions - the interaction of carbon-containing compounds with the furnace atmosphere during sintering (Fernandes et al., 2014). The pore size is related to the amount, shape and size of the foaming agent particles, smaller particles generate smaller pores (Lubas et al., 2017). Porosity increases with the amount of foaming agent and also if the particles show heterogeneity. If the particles are homogeneous and their concentration is low, then low porosity, pore size and permeability are achieved (Chakraborty et al., 2020). Time and temperature have a decisive impact on the properties and porosity, therefore the gas release process cannot be too long, as its complete removal from the structure is associated with an increase in density (Hakim et al., 2022). If the sintering temperature increases, the density and microhardness increase and the porosity decreases. The precipitation of crystals and the glass crystallization process itself increase the density of glass ceramics. The increase in strength resulting from the increase in sintering temperature is related to surface hardening and intensification of grain growth (Leenakul et al., 2016). As the sintering temperature increases, there is a sudden increase in volume shrinkage and a decrease in closed and open porosity (Dávalos et al., 2020).

Two groups of foaming agents are most important:

1. Inorganic: calcium carbonate, ammonium bicarbonate, ammonium oxalate, ammonium carbonate.
2. Organic: corn starch, cassava starch, rice husk, sawdust (Chakraborty et al., 2020), banana leaves (Arcaro et al., 2016), banana peel (Zaini et al., 2022), bamboo wood, lignin (Serna-Jiménez et al., 2021). The use of bio-waste from the agricultural or food industry as a source of foaming agents or main raw materials for the production of bioglasses and glass-crystalline biomaterials is intended to overcome the resistance of biomaterials to antibiotics and ensure greater biocompatibility and is becoming an economic necessity (Youssef et al., 2022).

5. CONCLUSION

Since the discovery of bioactive glass compositions, regenerative medicine has developed very rapidly, especially in the area of bone tissue engineering. Thanks to extensive research and knowledge of the human bone structure, as well as work put into understanding and improving bioglasses, it is possible to remineralize enamel, rebuild and fill numerous defects in cortical and trabecular bone. To cope with the problem related to the strength of amorphous structures, especially those that are porous and have a developed internal surface, glass-crystalline materials are being developed that have better mechanical properties and are more effective in places exposed to higher load-bearing forces. By understanding how composition affects the properties of bioglasses and knowing the effects of individual ions and oxides, by introducing changes and additions to the glass structure, it is possible to obtain materials that have the ability to deal with specific problems or diseases. Surface topography and ion release kinetics are important aspects taken into account when designing a biomaterial for tissue regeneration. The parameters of the porous structure can be largely controlled by controlling the manufacturing process. Foaming agents, as well as time, temperature and production method, is another factor shaping the structure of bioglasses, which should be examined beside with other factors.

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