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THERMOCHEMISTRY OF BIOLOGICALLY ACTIVE GLASSES

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Abstract

Mutual relation between thermal activity and biochemical activity of the phospho-silicate glasses which are used as controlled rate release fertilisers and bioglasses for medical applications, has been observed. Analysis of the local atomic interactions in the structure of glass is used to explain this relation.

Keywords: glass bioactivity, glass crystallisation, glass dissolution, glass structure, phospho-silicate glass

Introduction

Removing the effects of the disturbance of environmental equilibrium and of its degradation caused by uncontrolled development of technical civilisation has become one of the most important task at present. To realise this risk many different substances and materials of specific properties will be needed. Manufacturing ecologically–friendly materials (eco-materials) and substances intended to be used for environmental protection and environmental engineering is now a perspective trend in the industry.

In surgery and dentistry special materials biologically inert and tolerated by human body (bio-materials) have wider and wider applications (special steel, sintered alumina, ceramic tooth prosthesis etc.). Lately biologically active materials, able to participate in biological processes of living organisms (plants, animal and human bodies), have been elaborated [1]. Carbon fibres and carbon composites prosthesis resorbable by living organism or apatite ceramic and phosphorus containing glasses able to form bond with osseous tissue are the examples (bioactive materials) [2, 3].

Several inorganic glasses have biological activity and can be used as eco- and biomaterials. Thermochemistry and thermal analysis of bioactive glasses are the subjects of this study.

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Bioactive glasses

Bioactive controlled release rate fertilisers

Agriculture and gardening of today apply intensive mineral fertilisation. Each year considerable doses of nitrogen, potassium and phosphorus usually in the form of compounds of relatively high solubility are introduced into the soil. Microelements needed for cultivation are introduced also in the form of easily soluble compounds. Due to the considerable solubility of the mineral fertilisers, the high concentration of the useful components in soil does not always coincide with the period of their greatest demand on the side of the plants. As a result only a part of the mineral fertilisers is utilised by the plants or stored in the soil in an available form. A considerable amount of the components is washed out and the rest becomes immobilised in the soil in a chemically inactive and non-assimilative form.

The washed-out components are responsible for a marked disturbance of the biological balance in rivers and water reservoirs and the subsequent disadvantageous ecological changes. The consequence is the permanent need to supplement the content of nutrients by annual fertilisation.

These problems help to solve slowly acting fertilisers in glassy form. Phosphorus oxide belongs to compounds of strong glass-forming properties. Phosphate glasses in their composition accept many substances including considerable amounts of metal oxides. Owing to this property, it is possible to introduce via glass both the main components of fertilisers, i.e. potassium and phosphorus as well as microelements. The solubility of glasses in the soil environment can be controlled over a wide range by proper selection of their composition.

Glasses from the system K_2O–MgO–CaO–P_2O_5–SiO_2, which may function as controlled release rate fertilisers and self-controlled uptake of mineral components by the plants have been obtained. They also may be a source of the required microelements [1]. The glasses are not soluble in pure water but organic acids produced by plants roots easily extract useful components from them.

Glassy fertilisers could find application in areas where the use of easily soluble fertilisers is not effective enough. Regions where the soil is intensively washed-out by atmospheric or groundwater, water-logged areas and fenland sandy areas of high permeability as well as regions degraded by industry belong here. Lack of ‘salt effect’ is the advantage of these fertilisers and their are suitable for saline soils.

Slowly dissolving glasses are excellent means to feed colonies of algae or bacteria in biological sewage-treatment plants and other installations for environmental engineering.

Bioactive glasses for medical applications

In the studies of materials suitable for replacing the bones, the greatest attention is paid to materials, which – owing to the presence of phosphate and calcium in their composition – may release these elements under the influence of physiological fluids and form stable bonds with a living bone forming a kind of apatite structure. The first substance used for this purpose was hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and hydroxyapatite ceramics obtained by its sintering.

The first bioactive glass for surgery has been obtained by Hench [2] and it belongs to the most widely known bioactive materials of these groups. This is the silica, sodium-calcium glass of a composition modified by the addition of 1–10% of P_2O_5. The best known and most widely applied is the 45S5 glass containing 45% of SiO_2, 5% of P_2O_5, 24.5% of CaO, 24.5% of Na_2O (Bio-glass) [2].

In the search for materials of greater mechanical strength, attention has been paid to glass-ceramic materials, obtained by controlled crystallisation of glasses. There have been developed glass-ceramic materials, which, on account of their composition, may be formed as apatite-wollastonite materials (wollastonite $CaSiO_3$). They belong now to the more widely applied materials. The glass-materials Cerabone and Implant contain fluoroapatite and wollastonite in the glassy matrix. Owing to the presence of crystalline phases the material shows good mechanical properties (bending strength 215 MPa). It is obtained by sintering of glass powder [3].

The bioactivity of glasses and glass–ceramic materials is demonstrated through their ability to form in a living organism, in contact with osseous tissue, a layer of natural biological carbonate hydroxyapatite $[Ca_9(H_3O)_2(PO_4)_6(OH)_2][CaMg_{0.3}Na_{0.3}CO_3^{2-}\,cit_{0.3}]$, which bonds the bone and the implanted material.

Thermal reactions and thermal analysis of bioactive glasses

Glasses were obtained by melting the batches in a laboratory electric furnace at the temperature 1400–1550°C. Glass sand (SiO_2 99.9 mass% content), $MgCO_3$, $CaCO_3$, Na_2CO_3, K_2CO_3, $AlPO_4$, H_3PO_4 (85 mass%) of chemical grade purity were used as batch components of medical bioactive glasses. Minerals: apatite, serpentine and potassium ash were used in the glassy fertilizers production.

Glasses were melted in sintered alumina crucibles. The melt was poured on a cold steel plate as a 5 mm thick layer to be glassified. Transparent and quite homogeneous glasses were taken for investigations. Temperature gradient furnace was used for the study of crystallization of glass in a bulk. Rod-shaped samples were heated for 2 and 24 h. The degree of crystallization, phase composition, the shape and size of crystals in samples heated at different temperatures were determined. The samples were examined in XRD (DRON-3 apparatus), optical microscope and SEM with EDAX equipment (JEOL). IR and FTIR (Digilab apparatus) were used to control changes in the glass structure. Crystallization of powdered glass (0.3–0.1 mm fraction) was studied by DTA (Perkin Elmer DTA-7 apparatus).

Thermal analysis is indispensable in the investigations of the synthesis and the properties of bioactive glasses. The reactions occurring in glass batches containing as a component the phosphorus compounds differ from those occurring in batches for silicate glass (Fig. 1). A batch composed of $CaCO_3$, SiO_2, H_3PO_4 (liquid) (Fig. 1a) or $(HPO_3)_n$ (solid) (Fig. 1b) in the interval 100–350°C shows an intensive endothermic effect, connected with 20–40 mass% loss of mass. This result, from the formation of

Ca phosphates which is accompanied by the precipitation of CO_2 and evaporation of H_2O. In the interval 700–740°C there takes place the decomposition of acid phosphates, release of the appearing water and decomposition of Na_2CO_3. Simultaneously their intensive reaction with SiO_2 takes place. The developed compounds above 800°C form eutectic melt. In the presence of Na_2CO_3 in the batch, the eutectic melt appears at 870°C (Fig. 1c). The kind of the developed acid phosphates depends on the kind of the phosphoric acid used. For this reason, the loss of mass connected with their decomposition varies and accordingly the temperatures of the formation of their eutectics are different (Fig. 1).

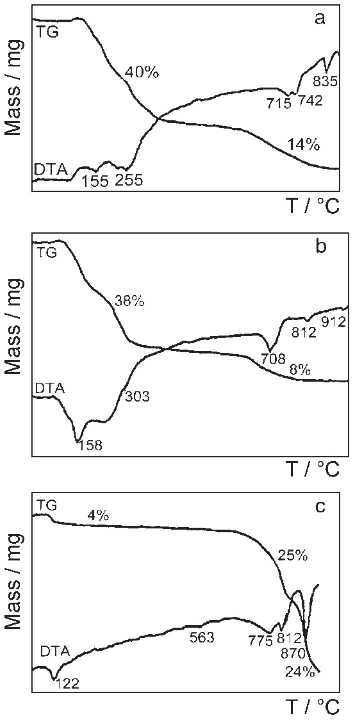

Fig. 1 Thermal analysis of batches for bioactive glasses

DTA and DSC measurements enable to determine the parameters characterising the thermal properties of the glasses. It includes the transformation temperature (T_g) which is the lowest temperature enabling the crystallisation of glass, and the softening point above which the glass has the consistence of a viscous liquid and crystallisation is not possible. The exothermal crystallisation peak (T_c) indicates the upper temperature of the thermal stability of the glass and the crystallisation heat, which is determined from it, is a relative measure of the participation of the glass components in the synthesis of the crystallising compounds and may be accepted as an index of the thermal reactivity of glass.

As it has been found, $(HPO_3)_n$, used as compound, which introduces P_2O_5 instead of H_3PO_4 for the synthesis of glass containing P_2O_5 (58.5), CaO (30), SiO_2 (10), CaF_2 (1.5) (mass%) causes considerable decrease (about 100 deg) of T_g temperature, and temperature of crystallisation. The kind of the phosphate used, as it can be seen, effects the formation of the phosphate clusters in the silicate network in the glass structure which, in turn, determines the thermal properties of the glass.

Crystallisation of bioactive phosphate-silicate glasses proceeds in several stages (Fig. 2). The particular crystallisation stages are usually visible on the DSC/DTA curves as separate exothermal peaks, which occasionally overlap. Thanks to this, DSC/DTA curves can be used to determine the heating temperature of the glass, required to obtain bioactive glass-ceramics of the desired phase composition.

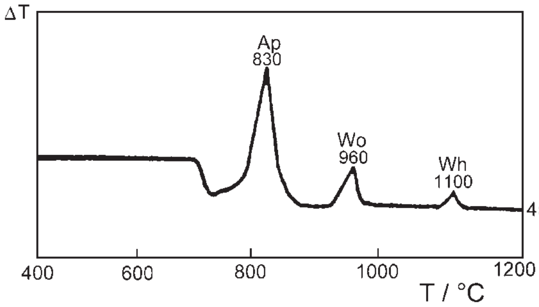

Fig. 2 DTA of multistage crystallisation Ap – apatite, Wo – wollastonite, Wh – whitlockite, glass ceramics

The kind of the crystallising compounds and the succession of their formation with increasing temperature depend on the chemical composition of glass. As it has been shown earlier [4] in glass containing Al_2O_3, as a rule, the first to crystallise are $AlPO_4$ and the calcium phosphates, and in the presence of a small content of P_2O_5 in the glass, the orthophosphates are formed. At a temperature close to the softening point the last to form are phosphates of a complex composition. Excess of SiO_2 with Na_2O and B_2O_3 (if they are present in the glass composition) form a glassy matrix in which the earlier crystallised compounds are stuck.

Thermochemical and biochemical activity of glass

The biological activity of glasses is estimated on the basis of their solubility and changes induced on the glass surface by solutions containing physiological fluids. A measure of the activity of glass fertilisers is their solubility in 2% solution of citric acid, which simulates the action of organic compounds released by plant roots to extract the useful components from the mineral fertilisers. HCl solution simulates the stomach acids, dissolving the glasses used as carriers of microelements in drugs.

The biological activity of glasses and glass-ceramic materials to be used as implants are determined by exposing them to the action of a simulated body fluid (SBF) of a composition corresponding to that human blood plasma (142.0 Na^+, 5.0 K^+, 2.5 Ca^{2+}, 1.5 Mg^{2+}, 103.0 Cl^-, 27.0 HCO_3^{2-}, 1.0 HPO_4^{2-}, 0.5 SO_4^{2-} in mM).

As it follows from the earlier investigations [5, 6], as for the action of these physiological fluids on bioactive glasses, its mechanism is similar, in spite of a different chemical composition of the particular fluids. Under the influence of these solutions, incongruent dissolution of glass takes place. In the case of acid solutions (the citric and hydrochloric acid) the hydrogen ions break the oxygen bonds of the glass framework causing their depolymerisation. The released silica precipitates in the acid solution, forming on the glass surface a layer of silica gel as a solid product of the process of incongruent dissolution, which binds a considerable part of the dissolving cation modifiers. There follows a gradual leaching of the cation modifiers from the layer of the silica gel.

The solubility of the phosphate-silicate glasses in the acid solutions used, increases with increasing the content of alkalies and P_2O_5 in the glass network, being on the other hand, resistant to the action of H_2O.

The bioactivity mechanism of calcium-phosphate and calcium-phosphate-silicate glasses, introduced into the human body as implants or prostheses is more complex. As it follows from 'in vitro' examinations, under the influence of SBF (pH of about 7), the glass dissolution takes place induced by the action of Cl^- ions on Ca^{2+} ions in the glass structure and the Na^+ ions on the oxygen bridges of the glass framework. The structure becomes destroyed which is followed by leaching of the Ca^{2+} and PO_4^{3-} ions as well as silica permeable as H_4SiO_4. The components leached from the glass and those deriving from SBF participate in the precipitation of new phases on the phase boundary. These are the tobermorite-like hydrated Ca-silicates, which are formed as a result of the corrosion of Portland cement by brines rich in NaCl. They form layers covering the glass surface [5]. Some researchers define it as a silica-gel layer [3]. On this layer the crystallisation of hydroxyapatite takes place, which, in contact with living osseous tissue, becomes rearranged into apatite of a composition and structure specific for this tissue. In the case of glasses with the composition of wollastonite $CaO{\cdot}SiO_2$ and CaNa-silicate glasses, which do not contain P_2O_5, hydroxyapatite is precipitated by the PO_4^{3+} anions present in SBF.

As it has been mentioned earlier, the bioactivity of glass fertilisers increases with increasing the content of P_2O_5 and K_2O. The thermal activity of these glasses expressed as the thermal effect of crystallisation increases in a similar order. For example, for glass containing 5 mass% of P_2O_5 and 5 mass% of K_2O it is equal to 100.2 J g^{-1} and it increases linearly up to 206.6 J g^{-1} for glass containing 15% of P_2O_5 and 10% of K_2O, with the temperature of crystallisation decreasing accordingly from 904 to 800°C. Detailed investigations of these glasses have been presented in [7].

A similar tendency can be observed in the case of calcium-silicate-phosphate glasses, the activity of which was examined by dissolving them in SBF. The highest temperature of crystallisation 908°C and the lowest enthalpy of crystallisation has been demonstrated by glass denoted as **a** (Fig. 3), containing 14.0 mass% of P_2O_5, 34.0% of SiO_2, 47.0% of CaO and 5.01% of MgO. A higher ability for crystallisation was demonstrated by the glass **b**, containing only 5.99% of P_2O_5, but as much as 24.55% of Na_2O, and additionally 44.97% of SiO_2 and 24.29% of CaO. The lowest crystallisation temperature (887°C) and the highest enthalpy of this process is characteristic of the glass **c**, containing the greatest amount of P_2O_5 – 25.6%, a great amount of Na_2O – 24.18% and 31.08% of SiO_2 and 21.62% of CaO.

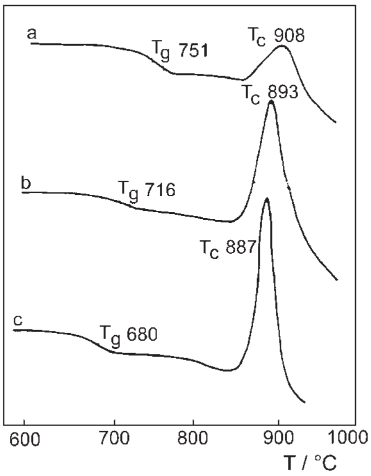

Fig. 3 DTA of bioactive glasses, T_g – glass transformation, T_c – crystallisation

The described parallelism of different processes such as the chemical activity in relation to the action of solutions and the thermal activity demonstrated by the formation of new compounds through a reaction between the glass components stimulated by thermal vibrations has its justification. They both have an identical initial stage. It is the depolymerization of the spatial structure of glass. The structural elements released in this way are able to rearrange and to combine into new compounds in accordance with their mutual chemical affinity. If the structure is destroyed step by step, the synthesis of new compounds takes place through several stages.

Bioactive glasses have polymeric structure, which network is build mainly by $[SiO_4]$ and $[PO_4]$ tetrahedra as network formers. They are joined apexes by common O^{2-} anions (oxide bridges). Some oxygen bonds between the network formers tetrahedra are broken by univalent (Na^+, K^+) or divalent (Ca^{2+}, Mg^{2+}) cations – modifiers.

The decay of the structure by thermal vibrations as well as by the action of biological fluids should run through the weakest chemical bonds. In the glass structure these are the ionic chemical bonds of the cations modifiers with the oxygen of the network and covalent–ionic bonds of the oxygen bridges in the network weakened by the internal strains. The strains are induced by the great difference in the covalency of bonds of the components combined by the oxide bridge.

In inorganic chemistry, Pauling's electronegativity and ionicity values are universally accepted as standardised characteristics of bonds and chemical interactions of atoms. A similar factors characterising crystallochemical properties of cations and atoms have been introduced by Görlich. This is the effective nuclear charge of atomic core, defined as $Z_{\mathrm{eff}}=\sqrt{I'_{\mathrm{V}}}$, where I'_{V} is the ionisation energy in the Rydberg units, needed to remove the v valence electrons from an atom. Its values are closely related to Pauling' electronegativity. The relative difference of the nuclear charge of the two bonding atoms constitutes the factor determining the ionicity of the heteropolar bond. The ionicity i_{G} or asymmetry of the chemical bonds between different atomic cores or ions, as cation–oxygen bond is measured by the relation $i_{\mathrm{G}}=1–Z_{\mathrm{eff1}}/Z_{\mathrm{eff2}}$, where $Z_{\mathrm{eff1}}< Z_{\mathrm{eff2}}$. Intrinsic affinity between two different atoms forming a heteronuclear compound is directly connected with the value of ionicity of a chemical bond [8, 9].

In the present study the ionicity value of bonds of the components atoms with oxygen (i_{G}) has been applied as a parameter characterising the strength of the bonds. It increases with decreasing ionicity. Another parameter is the 'localisation of the bonding electron' $L=\bar{Z}_{\mathrm{eff}}=\sqrt{Z_{\mathrm{eff1}}Z_{\mathrm{eff2}}}$ [9]. Its value increases with the covalence of the bonds with oxygen. This parameter has been accepted as a measure of the rigidity of the bonds.

Increase in the proportion of the non-directional ionic bond makes the structure flexible. Increase of the covalence of chemical bonds makes the structure more rigid, but simultaneously increases its strength. Ionicity of modifiers of the silicate glasses decreases in the following order K>Na>Ca>Mg. Network formers have ionicity below 0.500 and it decreases in the direction Al>B>Si>P.

The stability of polymeric structure of the oxide glasses is determined by the oxygen bridges. As a measure of the strength of oxygen binds, it is proposed to accept the difference in the value of i_{G} of the bonds with the oxygen of the cations joined by this oxygen (Δi_{G}). The difference in value L between these bonds (ΔL) is a measure of the internal strains in the oxygen bridges with not flexible, covalent bonds. The difference in i_{G} values (Δi_{G}) also supplies information in this case.

In the glass network built of the tetrahedra [SiO_4], and [PO_4] there appear bonds differing considerably in their ionicity. This refers, in particular, to Si–O bonds (i_{G}=0.428, L=2.410) and P–O bonds (i_{G}=0.314, L=2.640). Such a great difference in bonds (ΔL), which are rigid, due to the high degree of covalency (L>2.100) is responsible for the fact that in the oxygen bonds, joining both tetrahedra, considerable strains will appear, which makes the bonds breakable. That is why glasses with a two-component network SiO_2–P_2O_5 are of low stability.

An earlier study [10] revealed, that introduction of aluminium to phosphate glasses eliminates the P=O bonds and Si–O–P bridges are replaced by Al–O–P bridges. Then more stable links of [PO_4] and [SiO_4] tetrahedra by means of [AlO_4] are formed. The oxygen bridges Al–O–Si and Al–O–P formed then have their bonds less differing, then those in the Si–O–P bridge. However, a certain asymmetry of the bond is still retained, which results from the stronger interaction within the Al–O–P bridge (Δi_{G}=0.232) in comparison with Al–O–Si bridge (Δi_{G}=0.118) and the latter is easier to break. Thanks to this, the groups [AlO_4] [PO_4] can be released from the silicate network and the crystallisation of $AlPO_4$ takes place already near T_g, when the glass is heated (Fig. 4).

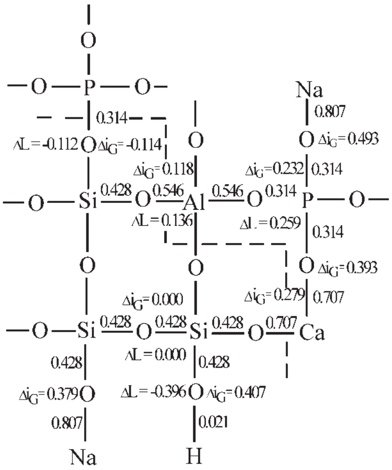

Fig. 4 Local atomic interactions in the structure of phospho-silicate glass and action of protonium (H^+) from bio-fluid, (dashed line indicates weakened oxygen bond of the glass network)

The release of phosphate domains of the network enables a simultaneous formation of crystalline calcium or calcium-magnesium phosphates. The chemical affinity of CaO to P_2O_5, expressed as the difference in ionicity of their bonds with oxygen (Δi_G=0.456) is much greater than for SiO_2 (Δi_G=0.279) and the bonds in oxygen bridges are correspondingly stronger (Fig. 4).

Action of H^+ ions from the biofluids, also breaks the weak oxygen bridges first. The H–O bond is characterised by the high covalency (i_G=0.021, L=3.153). H^+ is substituting cations – modifiers, of weak ionic bonds with network oxygens, and they are leached out. Joining H^+ to the oxygen of the network forming tetrahedron, makes the oxygen bridge extremely strained (ΔL= –0.396) and unstable. In this way protons from biofluides depolymerise the network and soluble silica and $[PO_4]^{3+}$ release to the solution. They form Ca-hydrosilicate and hydroapatite layer at the phase boundary. Similarly, Cl^- accelerates the dissolution of glass in NaCl containing liquids.

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