

Relaxation processes on intersurface of bioglass composite materials

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The basic problems one encounters when designing materials for medical applications are biocompatibility and mechanical properties. Recently, a development in the technology of composite materials has been observed. Bioactive glasses are used as a coating on porous corundum (good mechanical properties) implant materials. The technique used for producing glass components involves chemical routes, by the sol-gel process. The effect of a physiological solution on the surface properties of bioglasses and composites slightly differing in their chemical compositions has been examined by dielectric spectroscopy and DTA method. The temperature dependence of conductivity has been measured many times during the reduction and annealing processes, *i.e.*, at various reduction and relaxation stages. The layer formation and the type of electrical charge on the surface of an implant plays a significant role in the generation and remodeling of a bone tissue. Moreover, our measurements allow to preliminary identify the transport mechanism in the considered material.

Keywords: bioglass, biocomposite, dielectric spectroscopy, DTA.

1. Introduction

Nowadays there is a tendency to investigate the possibilities of combining various biocompatible materials into composites to receive final products of better strength and electric charge formation on insulating materials. The combination of the concept of the composite material with that of the graded material may open new opportunities for manufacturing biofunctional implants with better structure, properties and adjustment to the surrounding body cells [1]. A lot of research in the biomaterials field proved that due to introducing a bone implant a modification of an electric field associated with the bone surface could be achieved. The main feature of bioactive composite materials is their ability to bond chemically to bone through a biologically active layer of bonelike apatite [2]. At present, bioactive materials include some calcium phosphate compounds, bioactive glasses, bioactive coatings deposited on

ceramic or metal substrates. At body temperature, only two calcium phosphates are stable when the biomaterial is in contact with physiological solution. One of them is brushite, the second is hydroxyapatite (HA). WANG [3] indicates that biological apatites are similar to synthetic HA, but they differ from HA in composition, stoichiometry, physical and mechanical properties. The molar ratio Ca:P in enamel, in bone and in HA is 1.62, 1.65 and 1.67, respectively. The composites with graded structure may constitute the new group of implant materials. The bioactivity of glasses is connected with the formation and crystallization of HA layer on the material surface. This process is complicated and the necessary conditions are local saturation of simulated body fluid (SBF) with Ca ions in relation to apatite; the presence on the material surface of Si–OH groups favoring nucleation of HA; and negative charge of the material surface [4]. On the other hand, on the glass surface there exist many broken oxygen bonds, what in most cases leads to the negative charge in the bioglass [5].

Therefore, the purpose of this paper is to discuss the potential of dielectric spectroscopy and exoemission measurements as a means of characterizing the dynamic surface charge activity of the gel-derived CaO–SiO₂–P₂O₅ glasses reinforced by corundum.

2. Materials

2.1. Matrix

In agreement with earlier investigations [6, 7], the biogel glasses, of nominal compositions 36CaO, 60SiO₂, 4P₂O₅ (mol%), were obtained.

The basic gel was prepared from the mixture of: tetraethoxysilane TEOS – Si(OC₂H₅)₄; calcium nitrate tetrahydrate Ca(NO₃)₂·4H₂O dissolved in distilled water; triethylphosphate OP(C₂H₅O)₃, ethanol C₂H₅OH as an organic solvent, 2N natrium acid HNO₃ as a catalyst of the reaction of hydrolysis.

The basic composition of gel was prepared from this mixture with addition of Ca(NO₃)₂·4H₂O and OP(C₂H₅O)₃ and distilled water. The hydrolyzates were mixed for about 2 hours.

The gel was then subjected to controlled thermal processes; aged at 60 °C for 72 h, dried in an oven with the cycle ending at 120 °C.

The samples were soaked in SBF, an aqueous solution that has approximately the same ion concentration and pH as human blood plasma [8]. After soaking in SBF for various periods of time, the specimens were removed from the solution and dried in air.

2.2. Reinforcement agents

Submicrocrystalline sintered corundum is aluminium oxide (α -Al₂O₃) which can be an implant core of the ultradispersive structure received as a result of transforming

aluminium oxide sol into gel and modified with magnesium oxide (MgO). This allows us to obtain a specific structure of sinter containing short Al_2O_3 needles, separated by MgAl_2O_4 microthreads. Technologies offered by particular producers differ in the manner of producing Al_2O_3 sol and in the conditions of converting it into gel. At the moment one of the producers is American company 3M – and the product is known under the trade name Cubitron. Mechanochemical treatment (high energetic milling) leads to changing the material structure. The milling process took place in ethanol. Cubitron was added to the hydrolysate in 1:0.028 ratio. Then the hydrolysate containing submicrocrystalline sintered corundum grains (input granulation after 5, 10 and 15 hours of milling) was left in ambient conditions to be gelled, which occurred in a range of 7 to 14 days, depending on the quantity of water used. Dried gels were subject to preliminary heat treatment at 60 °C (in a drier) for 72 h, later for 72 h at 90 °C, and finally at 120 °C for 24 h (xerogel). Then they were heated in air at 2 °C/min speed to 800 °C and kept for about 2 hours.

After mechanochemical treatment for 5, 10 and 15 hours, the submicrocrystalline sintered corundum grains were examined by determining the size composition.

The size composition revealed that the distribution of differences in percentage shares of particular fractions (from $< 20 \mu\text{m}$ to $0.3 \mu\text{m}$) for 5-hour milling gets the form of the *t*-Student distribution, and for 10- and 15-hour milling it is the classical Gaussian distribution [9].

An optical microscope was used to observe the surface structures of the Cubitron reinforced bioglass films. Figure 1 shows that this material exhibits a mesoporous texture. On the surface, we can find two types of structure: porous structure on the left side of the sample and Cubitron grains (dark places).

Volume samples of bioglass composites (after gelling and heat treatment) created a gradient structure, visible macroscopically. For composites of unmilled grains two layers were clearly visible: the lower one, blue, containing most grains of Cubitron and the surface one, white, constituting bioglass. The surface side of all composites was clearly cracked. The main reason for cracking was an increase in the capillary

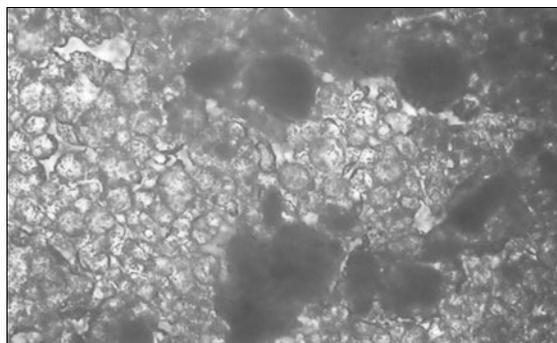


Fig. 1. Optical microscope image of bioglass film reinforced by Cubitron (10 h milling).

pressure made by the liquid in gel pores and the growth of surface tension of the liquid-steam system.

The unequal distribution of tensions led to cracking of material which was the result of creating in the sample volume the capillary pressure gradient connected with the limitation of transport of the liquid accumulated in pores [9].

2.3. Corundum-bioglass sandwich-type structure

The gelation of coated corundum implant substrates has been obtained by the deep-coating method. The details of preparing the samples were described elsewhere [10]. Corundum ceramic was produced by ROSIEK *et al.* [11].

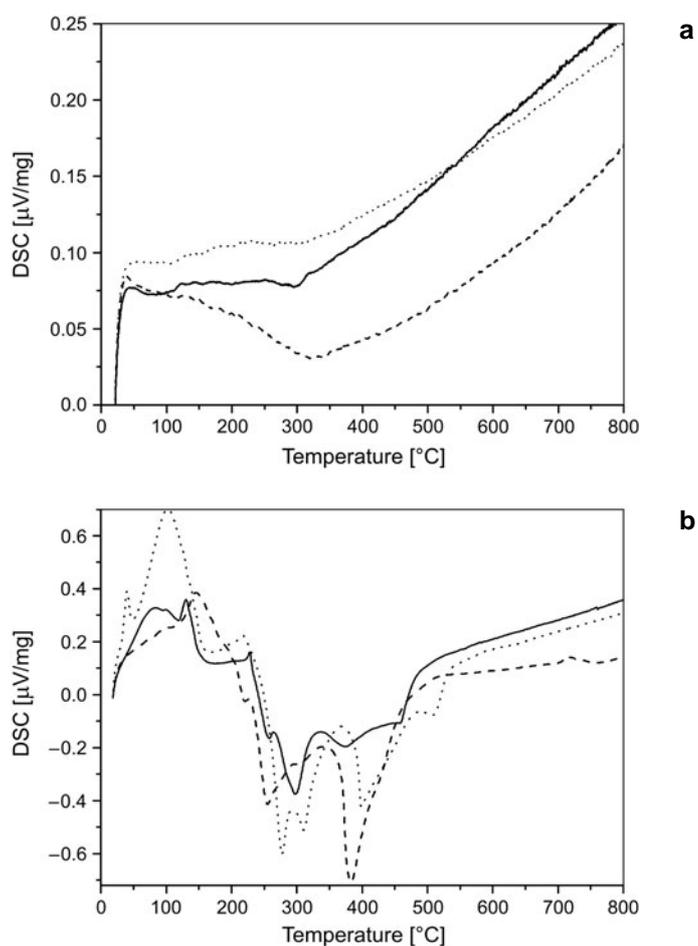


Fig. 2. Temperature dependence of the DSC signal for: bioglass-Cubitron composite powder sample heated at 800 °C – **a**, 120 °C heated biogel doped with milling Cubitron sample – **b**; (— 5 h, 10 h and ---- 15 h milling).

3. Methods, results of measurements and discussion

3.1. Differential scanning calorimetry (DSC)

A differential scanning calorimetry (DSC) method that identifies and distinguishes the surface from the internal crystallization processes in glasses has been developed. Materials were determined by the differential thermal analysis (DTA) performed using a NETZSCH DSC 404/3 differential scanning calorimeter with a S-type Pt-PtRh measuring head and standard platinum sample pans. An empty pan was used as a reference. DTA measurements were performed in atmospheric air under normal pressure. Heating rate in DSC was 5 °C/min. The sample temperature was measured with the accuracy of 5 °C.

The DSC curves for the bioglass composition prepared at 800 °C and reinforced by different grain sizes of Cubitron are shown in Fig. 2a as a function of the heat treatment temperature.

A completely different run of the DSC curve of the bioglass xerogel (dry in 120 °C) was observed in Fig. 2b. Figure 3 presents the temperature dependences of the DSC traces (a big change of the curve run) registered during the first heating run of the bioglass xerogel (dry in 120 °C). The first exothermic peak was observed at about 90 °C, the second one at 190 °C, and third at about 730 °C.

It has been shown by AGAMALIAN *et al.* [12] from the analysis of small-angle scattering and powder diffraction data that the silica glasses contain three types of adsorbed water on the porous surface, consisting of OH groups and chemisorbed water. The first type forms a physical adsorbed film which is desorbed during heating process at about 90 °C. The second type is a chemisorbed layer associated with spatially distributed molecules on the porous surface, which left the surface at above 190 °C.

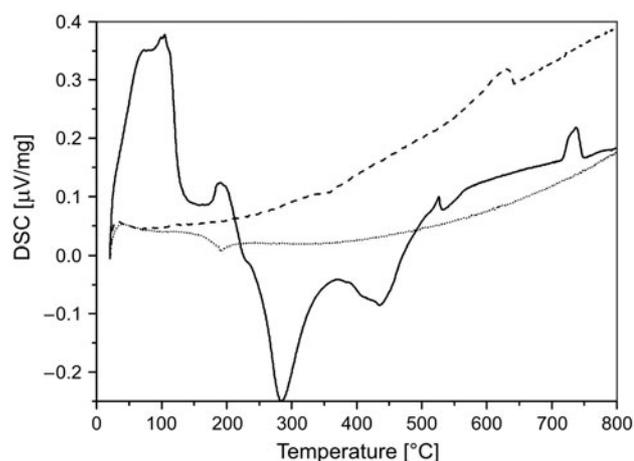


Fig. 3. Temperature dependence of the DSC signal for the bioglass–Cubitron composite powder of 800 °C heated sample (.....); bioglass xerogel dry in 120 °C (—); the second heating run of biogel (----).

These peaks completely disappeared in the second heating run or when the bioglass sample was preheated up to 800 °C. The 750 °C peak (changing the position in the second heating run) is probably connected with a chemisorbed water layer consisting of 40–60 molecules cluster connected to each other by hydrogen bonds. This type of peak was also observed in bioglass containing 15 hour milling powder of Cubitron. Probably, chemisorbed water molecules formed clusters near the centers distributed at the interface bioglass-small corundum grains.

3.2. Dielectric spectroscopy

Many works have been devoted to the studies of amorphous materials; the techniques employ higher frequency spectroscopies. Dielectric capacity measurements were performed with an Alpha-A High Resolution Dielectric analyzer. The frequency and temperature dependences of dielectric capacity were studied with Novocontrol Technologies. The system provides a frequency range from 10^{-3} Hz to 10^5 Hz, a maximum voltage of 1 V. The preliminary results for dielectric spectroscopy are showed in Fig. 4. In the case when we did not know the geometric size of the sample or could not give its definition, and also when the examined structure was a very unhomogeneous complex system, the capacity (not permittivity) could be measured [13]. Experimental investigations have established the relaxation response of insulators to be nonexponential in nature [14]. The violent change in the capacity of the xerogel biocomposite sample was observed in Fig. 4, at 40–90 °C. After heating the sample up to 110 °C, the capacitance run was stabilized. From Gutina's *et al.* investigations into dielectric phenomena, we can conclude that the porous silica surface demonstrated several relaxation processes [15]. The dielectric relaxation is

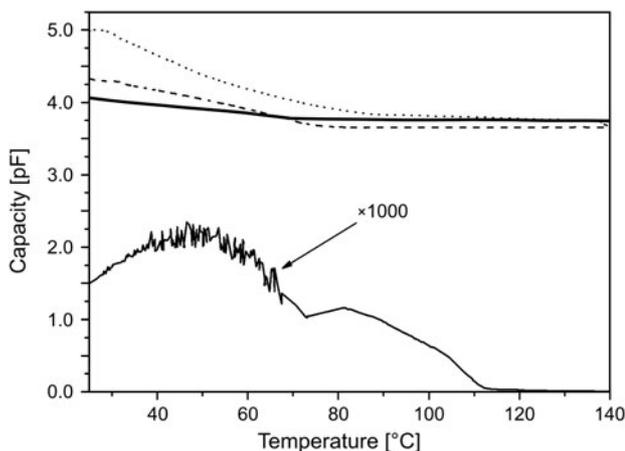


Fig. 4. Temperature dependence of the 1 kHz frequency behavior on the capacity of: ---- Al_2O_3 , — Al_2O_3 with bioglass (prepared at 800 °C), Al_2O_3 with bioglass (prepared at 800 °C) after SBF, and — Al_2O_3 with bioglass xerogel (dry in 120 °C).

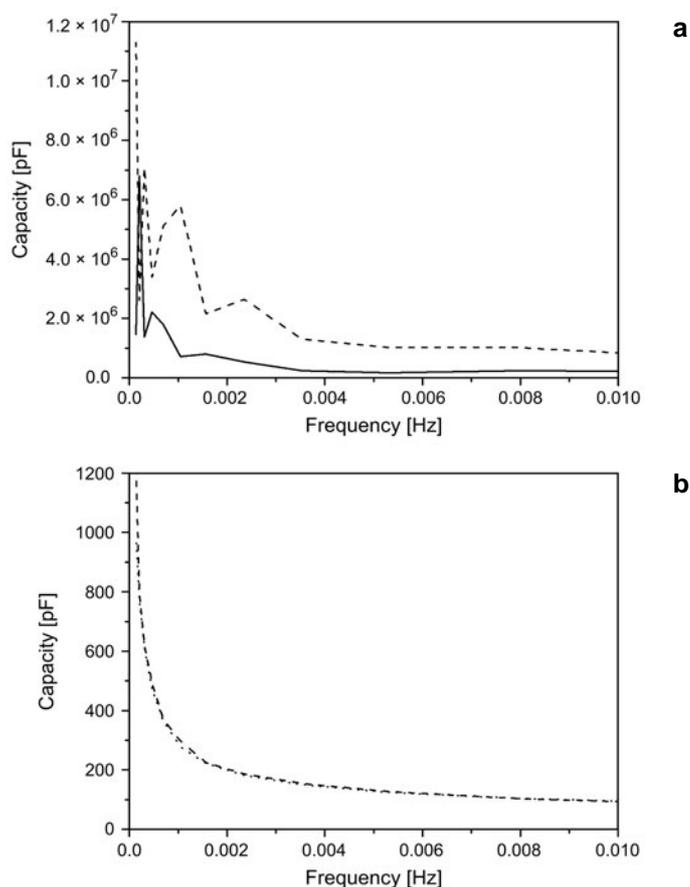


Fig. 5. Frequency dependence of the capacity for bioglass on corundum composite samples: ---- biogel on corundum (Al_2O_3 with bioglass xerogel (dry in 120°C)), — SBF soaked bioglass on corundum (Al_2O_3 with bioglass prepared at 800°C after SBF) – a; dry corundum sample, ---- biocomposite sample (Al_2O_3 with bioglass prepared at 800°C) – b.

associated with complex dynamics of water molecules and is due to their interactions with pore surface.

We observed three water peaks on the biogel-corundum composite samples and the bioglass-corundum sample in the low frequencies range is presented in Fig. 5a. In the same frequencies range for a dry biocomposite sample and corundum sample, we observed an increasing capacitance signal.

3.3. Optical stimulated exoelectron emission (OSEE)

The method of exoelectron spectroscopy is highly sensitive in the detection of defects on the surface and near surface layer.

The OSEE current was registered by a secondary electron multiplier (10^{-18} A) in a vacuum chamber with 10^{-4} Pa. Measurements of optical-stimulated kinetics were carried out with UV optical stimulation. As the parameters characterizing the OSEE decay curves are chosen, I_0 intensity of a slowly decaying component normalizes to the same quantity of the quanta of stimulating light. This method has been described elsewhere [16].

In Figure 6 we observe the decay curve of exoelectron emission from bioglass doped with the unmilling and 10 and 15 h milling Cubitron. The shape of the OSEE curves for bioglass doped with Cubitron grains is a typical decay curve of intensity, characteristic of many dielectrics [17]. These curves show an initial increase in emission and then a slow decay. The source of electrons are chemical interactions between the bioglass matrix and Cubitron dopants, which leads to the local deformation, microfractures or breaking of the bonds which can cause emission of the charge. The surface of aluminium oxide is a well known and stable source of exoelectrons. An electron transfer occurs from their occupied valence band into the free states of the intersurface.

The analysis of the results of measurements enables us to calculate, for different milling Cubitron doped bioglass composite materials, the parameters of the decaying component of the decay curve from the following equation:

$$I = \frac{N}{t_z} = \sum_i I_{0i} \exp(-\alpha_i t)$$

The value of α is a decay constant. In the Table the mean values of OSEE results of measurements are presented.

The comparison of the OSEE results (Fig. 6) for unmilling and milling reinforcing bioglass samples indicated that the grain size influenced electron emission. The milling process generated the surface charge on the small size grains of Cubitron (15 h milling) and then the charge accumulation and further breakdowns led to mechanical destruction and an increase in electron emission. The occurrence of electron discharges in a biogel sample is caused by the accumulation of the surface charge and contamination of the surface.

The glasses with a low content of SiO_2 and high density of nonbridging oxygen atoms have two exponentially decaying components of the emission current. A low value of surface charge for the modified glass (see Fig. 6) obtained by the OSEE method agrees with the earlier prediction that formation of a multilayer film structure gives as a result a decrease in charge of the surface [18]. The assumed interrelation between EE and migration cation vacancies can be explained as follows: when the cation vacancy meets a divalent ion (for instance O^{-2}), they would interact with each other, which results in the formation of a dipole. Since the cation vacancy has a negative effective charge, in order to preserve local electrical neutrality, an electron with the energy of dipole formation must leave this local region. It can also be emitted from the glass.

T a b l e. Mean values of OSEE results.

| Sample | α_i | I_{0i} |
|--|------------|----------|
| Bioglass reinforced by unmilling Cubitron | 0.02 | 0.62 |
| | 1.08 | 0.84 |
| Bioglass reinforced by 10 h milling Cubitron | 0.01 | 0.71 |
| | 0.21 | 0.80 |
| | 4.01 | 1.09 |
| Bioglass reinforced by 15 h milling Cubitron | 0.02 | 2.14 |
| | 0.27 | 1.79 |
| | 3.21 | 2.68 |

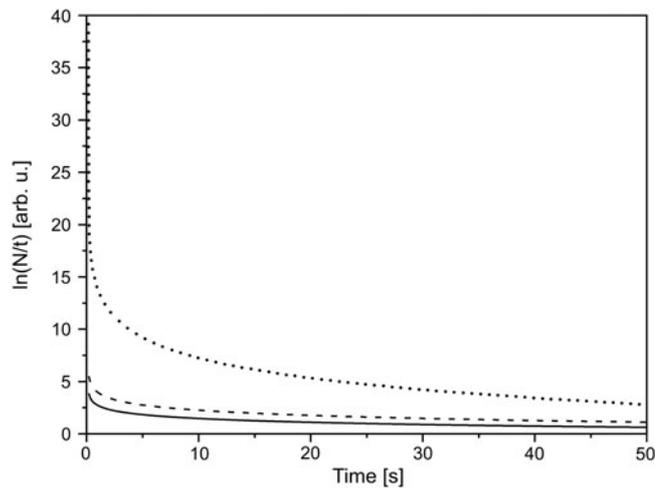


Fig. 6. OSEE decay curve for composite bioglass (..... bioglass with unmilled Cubitron, ---- bioglass with Cubitron milled for 10 h, — bioglass with Cubitron milled for 15 h).

These materials have conduction and valence bands with a mobility gap (energy gap) containing localized states which may act as charge traps. This explanation for releasing electrons is not the only possible one. In various cases, depending upon the state of the sample structure, different processes can be observed.

4. Conclusions

Basing on the investigation results the following conclusions can be drawn:

1. Volume samples of Cubitron-bioglass composites created a gradient structure.
2. Probably, chemisorbed water molecules formed clusters near the centers distributed at the interface bioglass-small corundum grains.
3. We observed three water peaks on the biogel-corundum composite samples and the bioglass-corundum sample in the low frequencies range of dielectric spectroscopy.

4. It was found that the dynamics of the generation of surface charge during UV-irradiation and the subsequent relaxation depended on the state of the composite sample.

5. Exoemission methods are sensitive for the fine surface changes of the bioglass doped with corundum grains.

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Received September 18, 2007