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Surface charge change kinetics of laser irradiated bioglass®

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In this paper, the influence of the UV and visible laser radiation as well as the simulated physiological solution on the surface of the bioglass® was examined. As the result of these processes a charged layer was formed on the surface of the glass. The method of measurements was based on exoelectron emission. The obtained results indicated that the electron trap in the bioglass® structure existed. The nature of these centres has been discussed.

1. Introduction

The materials, which are mainly applied in order to reduce disability and prolonge human life, are bioglasses®. Such materials were first produced by Hench in 1971 [1]. In the human body, we can apply only these materials, which have specific chemical, physical, mechanical and corrosion properties, assuring biocompatibility and long-term biostability. A surface structure of the bioglass resembles that of mineral phase of the skeleton, *i.e.*, calcium phosphate, and therefore exhibits a very good biocompatibility and bioactivity, but its mechanical properties are not satisfying. In the last years, the bioglass is used as the cover of metallic endoprotheses [2]–[4].

Previous investigations indicate that the thermostimulated exoelectron emission (TSEE) is a good tool to determine the surface glass properties because it is very sensitive to different surface defects, humidity, oxygen content and surface treatment [5]–[11].

The physicochemical concept of exoemission presented by Krylova is based on consideration of the dynamics of the surface processes. The breaks in chemical bonds due to excitation (like laser irradiation) of a solid, migration of resulting active particles, exothermic recombination accompanied by desorption, structural transitions and subsequent relaxation of stresses are the sequence of surface phenomena leading to exoemission [12].

MOTT and DAVIES [13] stated that the structural disorder of glass can result in some localized energy states in the forbidden energy gap. In glasses, a sharp limit between the forbidden energy band and conduction band does not exist; there is, however, a gradual transition from the energy states with the free carriers to the deep trap levels with the localized carriers.

Kortov and Zatsepin proposed a scheme of exoemission mechanism connected with the localized electron states in alkaline silicate glasses [14]. In the band gap,

there exist the tails of states which are characteristic of the band structure of glassy solids. In the edge of the conduction band of the silicate glasses, the alkaline ion states create the E_i-centres which are trapping electrons and therefore are the source of electron emission. The second type of defect centres are E'-centres which are the defects of the "break of bond" of silicon and oxygen vacancies.

These investigations concern the influence of the laser radiation on the charge of bioglass surface.

2. Experimental conditions

1. Measurements of TSEE were carried out with the point Geiger counter in the alcohol vapour over the free liquid surface co-working with the typical recording set.

2. The optical stimulated exoelectron emission (OSEE) current was registered by a secondary electron multiplier (10^{-18} A) in vacuum chamber with 10^{-4} Pa. Measurements of optically stimulated kinetics were carried out using 6 interference filters giving the wavelengths ranging from 225 to 325 nm.

As the parameters characterizing the OSEE decay curves were chosen, the maximum of OSEE intensity I_m normalized to the same energy of the incident quanta of the stimulating light and S_c surface charge: $S_c = \int_0^\tau I dt$.

3. Some samples were irradiated with Ar^+ laser (of wavelengths 488, 496 and 514 nm), while the others – with an N_2 laser (of wavelength 337 nm). Mean power per unit surface of irradiated samples was 160 W/cm^2 for all lines of Ar^+ laser. The N_2 laser was working in impuls system. Its repetition frequency amounted to 30 Hz, the pulse duration was 10 μs. Power per surface unit in each puls was about 10^5 W/cm^3 × puls.

4. The subject of investigations were two types of bioglasses produced by the Jelenia Góra Optical Factory (Poland) according to HENCH [1] with the following composition (percentage by weight):

45S5 45 SiO_2, 24.5 Na_2O, 24.5 CaO, 6 P_2O_5,

45S5.F 42.9 SiO_2, 23.4 Na_2O, 11.7 CaO, 16.3 CaF_2, 5.7 P_2O_5.

5. The samples were subject to an action of the simulating physiological solution with pH equal to 7.4 for two hours and 5 days. Li and Zhang reported that this ion-exchange process resulted in creation of a negatively charged surface [15].

3. Results and discussion

The TSEE curves for the UV N_2-laser irradiated samples are presented in Figure 1. We can observe the first maximum at about 375 K, higher for a 45S5 bioglass; the second one at about 580 K. The height of these maximum is about ten times bigger than that for unexcited sample. In the range of about 500 K, especially for the fluoride bioglass, it has been observed the appearance of an additional maximum which has not been stated in the case of the pure sample[6]. According to ARBUSOV [14], who obtained 360–380 K TSEE maxima for alkali silicate glasses, the nature

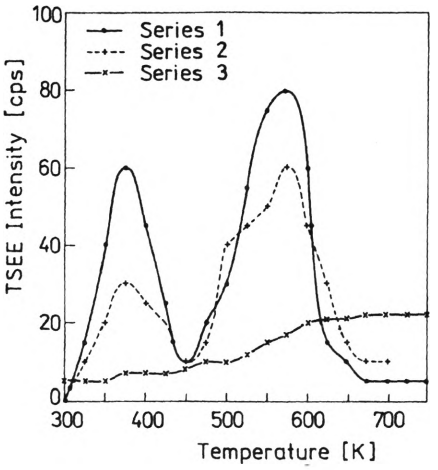

Fig. 1. Temperature dependence of TSEE intensity for bioglasses. Series 1 – 45S5, series 2 – 45S5F, series 3 – second cycle

of this centre is not definite. In a previous paper [9], it had been suggested that this peak was connected with the presence of the hydrated layer at the bioglass surface, because there was observed a violent change of intensity of this peak when the samples were immersed up to 2 h in the physiological solution. Based on IRRS-spectra, KIM [16] stated that these changes indicated that the amorphous calcium phosphate layer was converted into the apatite crystalline phase. Since in author's [7] previous investigations of another silicate glassses this peak was also present, the hydrated layer as a peak creation factor cannot be excluded. Perhaps two different electron centres are the sources of electrons. This maximum disappeared in the second cycle of measurements but irradiation restores the electron emission. The 580 K maximum may be associated with the decay of *E'*-centers [14].

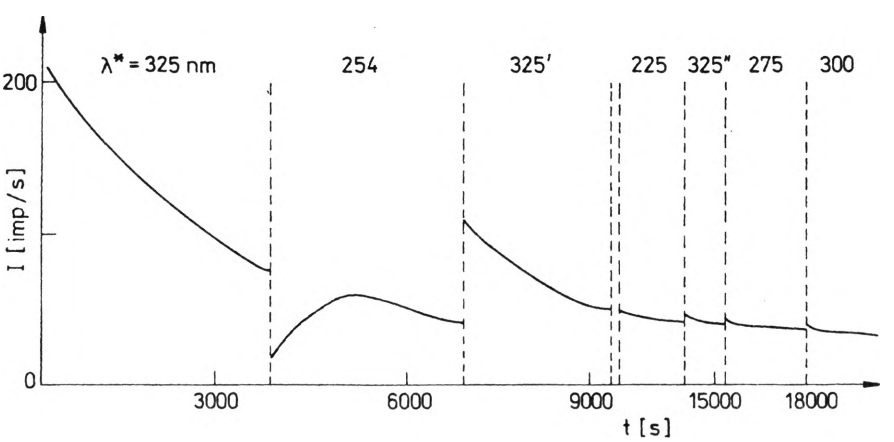

Fig. 2. OSEE decay curve for 337 nm laser excitation bioglass® sample, λ^* is stimulation light

In Figure 2, there are presented the OSEE decay curves for the 337 nm (3.7 eV) laser excited bioglass sample. We can observe the very fast decay of electron emission as a result of irradiation with 325 nm stimulation light. The different shape of decay curve for the 254 nm (4.9 eV) was similar to that obtained for the bioglass® being immersed in simulation physiological solution [10]. This energy of photons corresponds with an average dissociation energy of water (4.8 eV) and maybe this process is a source of exoelectrons in this energy range. The glasses with the low content of SiO_2 and high density of nonbridging oxygen atoms have two exponentially decaying components of the emission current. The existence of this decay curve for an excited sample can be explained by ionization of the filled localized states of

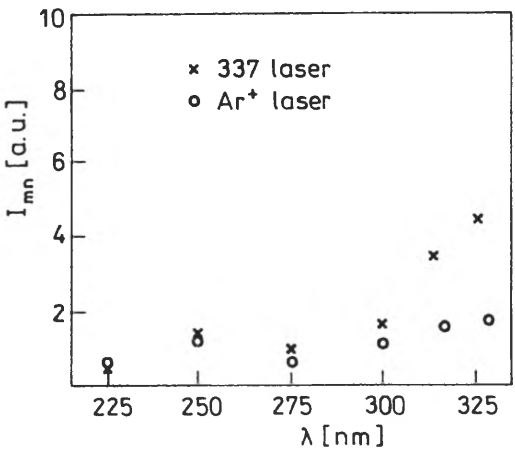

Fig. 3. Dependence of normalized intensity of OSEE on the wavelength for laser irradiated bioglass®. × 337 laser, o Ar^+ laser

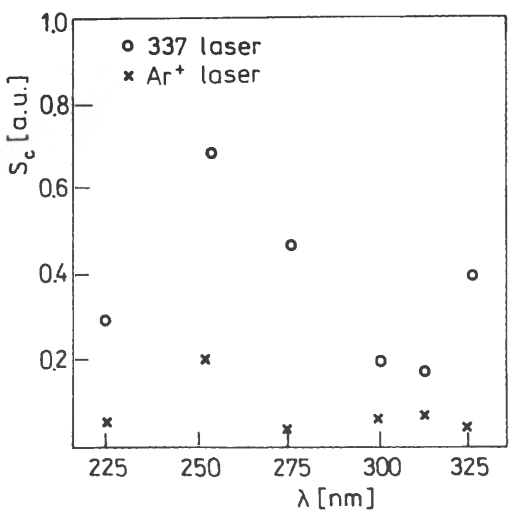

Fig. 4. Dependence of surface change of OSEE on the wavelength of stimulation light after 5 days of 45S5.F bioglass® immersion in physiological solution. o 337 laser, × Ar^+ laser

UV-radiation. This radiation can stimulate the exoelectron emission from the valence band into the energy range where the nonbridging oxygens are situated [14].

In Figure 3, there is presented the dependence of the normalized OSEE intensity on the wavelength for the sample irradiated with 337 nm nitrogen laser and kept for 2 h in physiological solution sample. We can observe a small maximum at about 254 nm and then the monotonical increase in the direction of longer wave to the 325 nm. After an irradiation with the argon laser, we obtained the curve of the same shape, but its value in 275–325 nm range was much smaller. The shape of the curves for 514, 496, 488 nm was the same in the limits of the experimental error. The source of these exoelectrons may be a phase transition.

The change of the surface charge of the fluoride bioglass® irradiated with 337 laser and kept for 5 days in simulated physiological solution is presented in Fig. 4. The maximum of the surface charge value, about 250 nm, is probably connected with the absorption of water by fluoroapatite and formation of HPO_4^{-2} ions in the structure [17]. Formation of these ions in apatite bonding layer may contribute to the difference in bond strength between the fluoride and non-fluoride bioglass®.

4. Concluding remark

Exoemission measurements indicate that the laser irradiation leads to filling of the electron traps present in the bioglass structure. In this paper, the nature of these centres is discussed.

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