

BIOACTIVE BLACK GLASSES AND THEIR MODIFICATION WITH CERIUM

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Introduction

Black glasses are interesting novel materials based on amorphous silicon oxycarbide (SiOC). Their structure may be compared to the structure of amorphous silica ($v\text{-SiO}_2$) in which some of the oxygen atoms are replaced by the carbon atoms. Because of the difference in the chemical character between these two elements, two atoms of oxygen are equivalent to one atom of carbon. It is causing the local densification of the structure of the original material and then the improvement of the performances in comparison to the amorphous silica. Stronger network increases the mechanical and chemical resistance, thermal stability and electrical resistivity. In addition, the resistibility to oxidation of the silicon oxycarbide is higher than in the case of silicon carbide. Obtaining of black glasses is challenging due to the crystallization of SiC and controlling of the amount of the free carbon. The most effective way of performing this material is the sol-gel method. It allows the introduction of silicon-carbide bond directly to the precursors by the use of modified alkoxysilanes. The Si-C bond is kept during reactions of hydrolysis and polycondensation and subsequently transferred to the final material. Its presence may be proved after ceramization confirming the efficiency of the proposed method [1]. Properties of black glasses make them perfect materials for protective layers working in hard conditions, for example, in the fuel cells and the catalysis industry and moreover as a biomaterial. The deposition of the SiOC coating may be performed by the dip-coating or EPD methods, which allows the creation of the homogenous and continuous layer on the chosen surface without shape restrictions. The used method of synthesis allows various modifications. One of the most interesting one is the modification with cerium. This rare-earth metal in the form of Ce^{3+} ions may replace Ca^{2+} ions in the hydroxyapatite unit cell. It is due to the similar electronegativity and the ion radius. Moreover, cerium is known as an inhibitor of corrosion and has some antibacterial and fungicidal properties. It is not required that the cerium must be bonded into the glass matrix, it may appear as the nanoparticles of its salts or oxide [2-4].

Materials and Methods

Black glasses were obtained via the sol-gel method. The hydrolysis and polycondensation was performed with the use of methyltriethoxysilane and dimethyldiethoxysilane, which were introduced to the material Si-C band through T and D structural units in the proper ratio. Cerium was introduced to the sol by the addition of cerium nitrate. Obtained sols, with and without Ce, were deposited on the metallic, steel and titanium, with the use of dip-coating method. The chosen speed of the sample movement was established to 20 cm per minute. To obtain the proper thickness of the layer, process was repeated three times. Samples were dried 7 days and then ceramized in 800°C in the protective atmosphere of inert gas – argon. The bioactivity of the material was examined by performing the so-called Kokubo test [5].

The obtained material was examined by thermal methods, such as thermogravimetry and calorimetry, X-ray diffractometry, infrared spectroscopy, Raman spectroscopy and scanning electron microscopy with the energy-dispersive X-ray spectroscopy compartment.

Results and Discussion

The study of the structure proved that the obtained materials were amorphous and contained Si-C bond and may be called black glasses. The addition of the cerium caused the phase separation of the cerium oxide in the form of nanoparticles without changing the matrix material. After performing the Kokubo test, the white residue was discovered. SEM examination showed the spherical forms characteristic for the hydroxyapatite's morphology (FIG. 1). The presence of this calcium phosphate was confirmed with the EDX analysis. FIG. 2 presents SEM microphotograph of the surface of the untreated black glass modified with cerium. It is clearly confirming the similarity between the hydroxyapatite and the cerium oxide nanoparticles with its morphological figures.

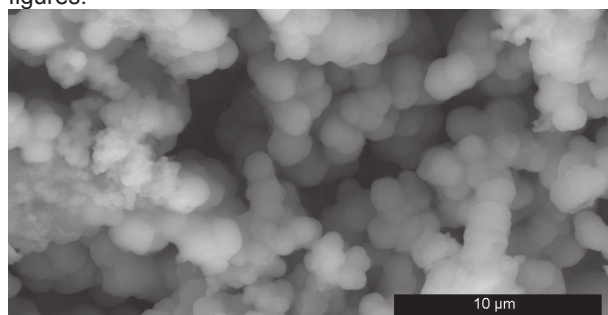


FIG. 1. Hydroxyapatite residue on the surface of the black glass after Kokubo test (SEM microphotograph).

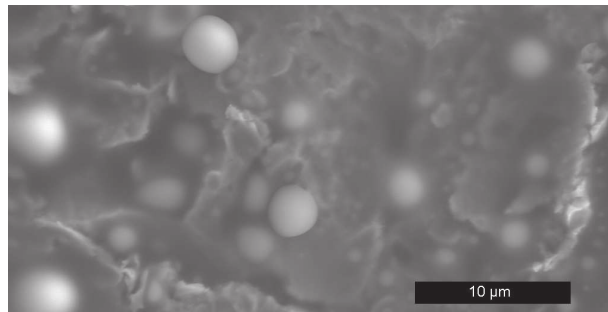


FIG. 2. SEM microphotograph of the surface of the cerium-doped black glass.

Conclusions

The performed experiment and examination proposed promising modification of the known bioactive materials which were black glasses by doping them with cerium. It was done to increase the bioactivity and protective properties and to add new antibacterial and fungicidal characteristics.

Acknowledgments

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