

CORROSION PROPERTIES OF CALCIUM-BISMUTH-BORATE GLASSES WITH SILVER

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Abstract. Quaternary $\text{Ag}_2\text{O-CaO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses are investigated with regard to release behaviour and local structure. The dissolution behaviour in water and physiological serum shows that the cations are released rapidly or gradually and points out a multi-step process, generally characterised by higher rates in water than in physiological serum. The structural effect of silver addition to bismuth-borate glasses is observed from infrared spectroscopic data. The antibacterial activity of the investigated samples was tested on five bacteria.

Key words: corrosion, oxide glasses, microstructure, silver.

INTRODUCTION

Over the past two decades a general experimental and theoretical framework has been developed for understanding the corrosion behaviour of glass in diverse environments [5]. Novel systems allowing controlled release of components are intensely investigated [1]. Various inorganic antibacterial materials containing silver have been developed and some of them are in commercial use. More chemically durable materials, which slowly release the silver ion for a long period, are developed for medical applications. The silver ions are rapidly released or they can be gradually released into the water at a controlled rate and show an excellent antibacterial property [10]. Silver is capable of killing over 650 different forms of bacteria, viruses, *Candida*, and molds [14]. Bismuth trace element is used for eye/ear infection and sore throats. The antibacterial activity of bismuth is also known [4]. Although boron is potentially toxic to all organisms, and, as boric acid and borax, has been used as a pesticide and food preservative, higher animals usually do not accumulate boron because of their ability to rapidly excrete it [13]. It appears that boron may influence the production of hormones (including the active form of vitamin D), improve brain and psychological functions, and exert

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immune-boosting activity [15]. Calcium is an essential element entering into the cell walls and bones. It is important for blood clotting and it is implied in the complicated mechanisms of long-term memory and learning [3]. The composition and local structure at the surface of the samples is of great importance in their dissolution properties.

The aim of this paper is to investigate the dissolution behaviour and the antibacterial effects of quaternary $\text{Ag}_2\text{O}\text{-CaO}\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses in correlation with their microstructure.

MATERIALS AND METHODS

The investigated samples belong to $x\text{Ag}_2\text{O}\cdot(5-x)\text{CaO}\cdot 10\text{Bi}_2\text{O}_3\cdot 85\text{B}_2\text{O}_3$ system ($1 \leq x \leq 4$ mol %). They were obtained from homogenized mixtures of AgNO_3 , CaCO_3 , $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ and H_3BO_3 p.a. chemical reagents by melting at 1050°C for 15 minutes in sintered corundum crucibles in an electric furnace and quickly undercooling at room temperature by pouring onto stainless steel plates. All as prepared samples were transparent and colourless.

The corrosion behaviour was followed in static regime by immersion of disk samples in different solvents (desalinated water, physiological serum and chlorine acid solution with $\text{pH} = 1.5$) by measuring the mass of samples maintained in the incubation solutions at 40°C for different times up to 68 hours. The samples mass was determined by using an analytic balance sensitive to 0.1mg. The glass surface area to solution volume ratio was around 15 m^{-1} for all samples. The dissolution rate, DR, was calculated [9] from the measured mass loss Δm (g), samples surface area A (cm^2) and the immersion time t (min) using the equation $\text{DR} = \Delta m / (A \cdot t)$.

IR spectra were recorded at room temperature from powdered glass samples pressed in tablets with KBr, in the wave number range $400 - 4000\text{ cm}^{-1}$, using a UR-20 Carl Zeiss spectrophotometer with a resolution of 0.6 cm^{-1} at 1000 cm^{-1} .

The sensitivity of different bacteria to the released components was tested in aerobiosis, by use of nutrient agar plates with wells filled with powdered glass samples. Gram-positive (*Streptococcus* sp, *Bacillus* sp, *Bacillus anthracis* strain R 1190) and Gram-negative (*E. Coli*, *Salmonella* sp. and *Pseudomonas pyocyanea*) bacteria were inoculated on the agar surface. Diameters of the growth inhibition areas were determined in cm, after 24 hours incubation at 37°C .

RESULTS AND DISCUSSION

The results of the corrosion test carried out in water and physiological serum are shown in Figures 1 and 2. The dissolution rate decreases in water from the average value $5\text{ }\mu\text{g}/\text{cm}^2\cdot\text{min}$ to $0.5\text{ }\mu\text{g}/\text{cm}^2\cdot\text{min}$ as the Ag_2O content in sample

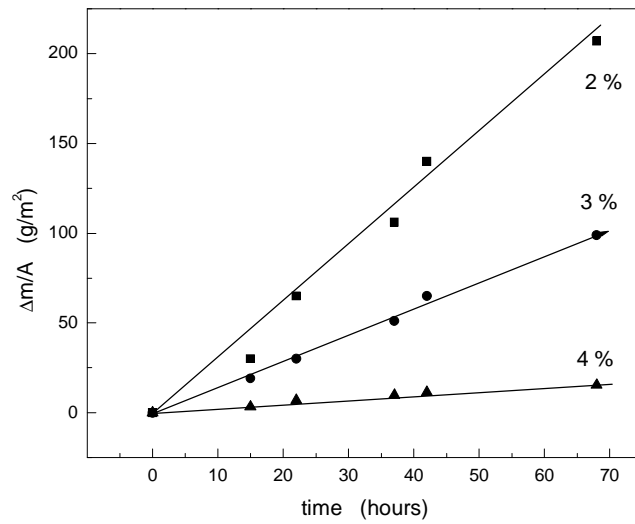


Fig. 1. Time dependence of specific mass loss in water from $xAg_2O \cdot (5-x)CaO \cdot 10Bi_2O_3 \cdot 85B_2O_3$ glass samples. The lines are only guide for eyes.

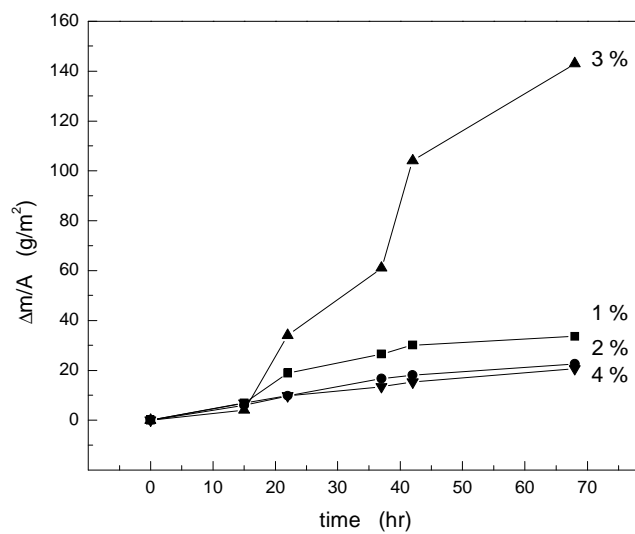


Fig. 2. Time dependence of specific mass loss in physiological serum. The lines are only eye guide.

increases from 2 to 4 % mol, while in physiological serum the DR values are constant lower, under $1 \mu\text{g}/\text{cm}^2\cdot\text{min}$, excepting the sample with 3 mol % Ag_2O for which $\text{DR}_{\text{av}} = 2.6 \mu\text{g}/\text{cm}^2\cdot\text{min}$. Mass losses could not be measured after immersion in HCl solution because all samples softened in the first 15 hours.

Some data concerning the releasable cations of the investigated samples, which are of interest with respect to role they could play in oxide glass systems, are summarised in Table 1. The cationic field strength is expressed by the ratio of the cation charge to the square of the ionic radius and is an indication of relative bond strengths. The cations belonging to the conventional glass former oxides are characterised by high field strengths as compared to the cations entering as modifiers. Both calcium and silver ions act as glass network modifiers. One also remarks that Ca^{2+} and Ag^+ have very close values for ionic radii but they considerably differ with respect to their relative bond strengths.

Table 1.

Coordination number, ionic radius, field strength, Pauling electronegativity and single bond strength for the cations [7, 11, 16] entering $x\text{Ag}_2\text{O}\cdot(5-x)\text{CaO}\cdot 10\text{Bi}_2\text{O}_3\cdot 85\text{B}_2\text{O}_3$ glasses.

Cation	Coordination number	Shannon ionic radius (Å)	Cation field strength (Å ⁻²)	Electro-negativity (Pauling units)	Single bond strength M-O (kJ·mol ⁻¹)
B^{3+}	4	0.25	48	2.04	808.8 ± 20.9
	6	0.41	35.69		
Bi^{3+}	6	1.17	2.19	2.02	337.2 ± 12.6
	8	1.31	1.75		
Ca^{2+}	6	1.14	1.53	1.00	402.1 ± 16.7
	8	1.26	1.26		
Ag^+	4	1.14	0.77	1.93	220.1 ± 20.9
	6	1.29	0.60		

The structural units built around the glass former cations can be evidenced by vibrational spectroscopy. The IR spectra (Fig. 3) show a strong band around 700 cm^{-1} assigned to the B-O-B bending vibrations and some very weak ones appearing around 800 and 1250 cm^{-1} which could be attributed to the BO_3 triangular unit vibrations. The BO_4 unit vibrations [6, 8] were recorded from all samples between 900 and 1100 cm^{-1} . This result denotes that the change of the boron coordination from BO_4 to BO_3 units is insignificant in the investigated composition range. The weak infrared bands in the $500\text{--}670 \text{ cm}^{-1}$ spectral range was correlated with the presence of $[\text{BiO}_6]$ octahedral [2, 12].

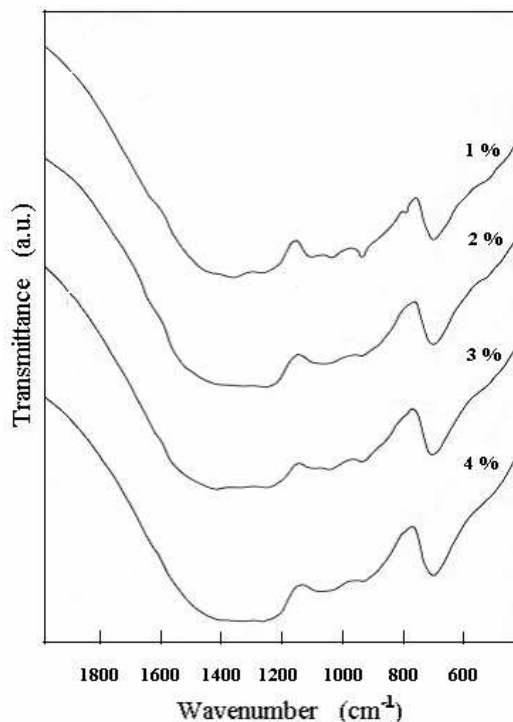


Fig. 3. The IR spectra recorded from $x\text{Ag}_2\text{O}\cdot(5-x)\text{CaO}\cdot 10\text{Bi}_2\text{O}_3\cdot 85\text{B}_2\text{O}_3$ glass samples.

The sensitivity of different bacteria to the released components was evaluated based on the growth inhibition diameters (d) after 24 hours of incubation. A more pronounced inhibitory effect is being observed for Gram negative bacteria than for Gram positive ones. The results evidence that the bacterial sensitivity depends on sample composition. A somewhat lower antibacterial activity of the sample containing 4 mol % Ag₂O might be due to the higher dissolution stability of the corresponding glass as showed by corrosion tests.

In order to explain the different release of cations from the glass network in the investigated dissolution media, beside the composition of glasses and solvents is necessary to take into account the short-range order characterising the samples.

The structural stability of cations in glass matrices is correlated with their local symmetry. The local order in glass and crystalline compounds of the same composition has both similarities and differences. The differences are assigned to the loss of long range order, to the deviation from a perfect crystalline structure. The atoms arrangement in the first coordination sphere is determined by the chemical composition and peculiarities of chemical bonds and generates the local order around them, that is very important to depict the vitreous systems.

CONCLUSIONS

The IR results show that the local structure of the investigated samples preponderantly consists of tetracoordinated BO_4 units. BiO_6 structural units were also evidenced. The silver addition to the calcium-bismuth-borate host glass preserves the vitreous structure, evidencing high ability to accept a relatively large Ag_2O content.

The dissolution behaviour of $x\text{Ag}_2\text{O}\cdot(5-x)\text{CaO}\cdot 15\text{Bi}_2\text{O}_3\cdot 85\text{B}_2\text{O}_3$ vitreous system in water and physiological serum indicates a multi-step process generally characterised by higher rates in water than in physiological serum. The addition of Ag_2O to the lime-bismuth-borate matrix influences the dissolution rate of samples.

The antibacterial effect of the released cations is more pronounced on Gram-negative bacteria. The magnitude of this effect is in agreement with the cations release rate. The results evidence that the bacterial sensitivity depends on sample composition. A somewhat lower antibacterial activity of the sample containing 4 mol % Ag_2O might be due to the higher dissolution stability of the corresponding glass as showed by corrosion tests.

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