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Study of historical lead silicate glasses and their preservation by silica coating

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ABSTRACT

In the last years the interest for protection of the historical objects has increased. Among them a high number of ancient and middle age objects were made from lead silicate glasses. Such historical objects from glass contain small quantities (below 5 wt%) of transitional elements as Cu, Ag, Fe, which decrease their resistance at weathering. Previous investigations show that protective sol–gel silica coating does not change the appearance of artistic alkali silicate glasses when it is deposited on their surface. In the present paper model lead silicate glasses with compositions similar to ancient objects were studied. Their chemical resistance in water, morphology and structure was investigated, being established that the iron added into glass changed the corrosion mechanism. In order to prevent the weathering of the synthesized glasses, a protective thin film was applied on surface. All glasses show a better resistance at water attack after coating with a film of silica gel.

1. Introduction

The historical objects made by glasses can be classified as lead containing glasses or alkali silicate glasses [1–17]. In the last years the interest in preservation of historical objects increased. The degradation of historical glasses was mostly related with the action of rain, gases or moisture from atmosphere on their surface.

Lead glasses were intensively used as ornaments, cups, or jewelry in historical and middle age for their beautiful colors and transparency. Lead silicate glasses were found especially in Japan and China. In the ancient times different metals were added in historical glasses for obtaining of beautiful colors but without consideration for their chemical resistance. The study [18] developed on the ancient glasses demonstrated that the increase of lead determined a color shift from a turquoise-blue tint to an emerald-green hue. Different clay minerals and silver nitrate mixtures were generated yellow color in ancient glasses [19]. The addition of manganese atoms lead to decolorized samples [8].

Few groups of researchers [9,14,18,20–25] found methods to preserve the ancient and middle age glasses. The historical glasses as ancient stained glasses [22,23] and medieval stained glass windows [9] have compositions of potash-lime; soda-lime and potassium–magnesium silicate glasses. The appearance of artistic alkali silicate glasses does not change when silica coating was deposited on their surface [9,14,17]. Bianco [13] studied protection of ancient stained glass with 6–15% at metallic Pb inside. The results of ageing tests have been shown the efficiency of H^+ and Pb^{2+} catalyzed coatings and the inefficiency of the non-catalyzed sol–gel layers in case of glasses with metallic lead in compositions [13].

The present work proposes the study of behavior at water attack during resistance tests of model lead silicate glasses containing small quantities of transitional elements (Fe_2O_3, CuO and Ag_2O) before and after coating with a silica thin film. In a previous paper the characterization from structural and thermal point of view of lead silicate glasses that reproduced the composition of the ancient ones was reported [26]. In a second paper the beneficial influence of silica coatings on the surface of historical alkali silicate glasses was studied [25].

2. Experimental part

2.1. Glass preparation

In order to establish the experimental conditions required to protect historical objects lead silicate glasses with similar

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Table 1
The composition of the ancient glasses [27].

Chemical composition (wt%)							
SiO_2	PbO	CuO	Ag_2O	Fe_2O_3	Al_2O_3	CaO	MgO
29.00	70.00	0.54	0.14	0.22	0.03	0.07	0.02
28.00	66.00	0.10	0.16	0.19	0.06	0.32	0.02
29.20	71.20	0.28	–	0.08	0.08	–	0.05

Table 2
Oxide compositions of obtained glasses and their aspect and color [26].

	Chemical composition (wt%)					Observations
	SiO_2	PbO	CuO	Ag_2O	Fe_2O_3	
Glass 1	30.00	70	–	–	–	Transparent and Light Yellow
Glass 2	29.50	70	0.5	–	–	Transparent and Dark Green
Glass 3	29.35	70	0.5	0.15	–	Transparent and Light Yellow
Glass 4	29.23	70	0.5	0.15	0.12	Transparent and Dark Yellow

composition were prepared. In Table 1 three compositions of ancient lead silicate glasses from Japan are presented [27]. As can be seen their composition is close to eutectic composition $SiO_2 \cdot 2PbO$ from binary system.

In order to study the influence of transitional metal oxides on the chemical stability of glasses the eutectic composition was selected as reference and other three compositions of glasses with additional oxides were proposed. The studied glasses are presented in Table 2.

The samples that reproduced historical glasses were prepared by traditional melt quenching route. The synthesis route was described in a previous paper [26]. Starting materials were PbO, SiO_2, CuO, $AgNO_3$, Fe_2O_3 (Merck). The melting of starting materials, in appropriate compositions, was performed at 1400 °C, for 1 h in electrical oven. The glasses were cast in carbon mold and thermally treated at 300 °C, for 2 h.

2.2. Sol-gel silica coatings

The challenge in the coating process for the protection of historical glasses is that chemical composition of glasses may not be compatible with the proposed film coating composition. The lead silicate samples were coated with thin films of silica obtained by sol-gel route. We supposed that because the lead oxide and silica can be mixed in any percentage in glasses; a thin film of silica gel deposited on the glass surface will be highly protective without aspect deterioration.

The solution used for coating have been prepared starting from TEOS (tetraethyl ortosilicate) $[Si(OC_2H_5)_4]$, ethanol, distillated water and hydrochloric acid. The solution with molar ratio C_2H_5OH:TEOS:H_2O:HCl $=10:1:3:0.03$ was prepared according with literature data [13,14,28]. Previously, the glass samples have been cleaned with detergent solution and distilled water, and then in ultrasonic bath for 3 min in ethanol. The deposition of protective silica coatings were performed by dip coating, with an immersion and withdraw rate of 50 mm/min and 60 s as time to remain in solution. The coated glasses were dried in air at room temperature.

In this work the authors wished to increase the chemical resistance using a silica protective film. Taking into consideration that silica is also the one of the main oxide in the composition of the ancient glasses investigated and the thickness of the film is very low (below 1 μm) it was assumed that it will not damage the artefacts. The film composition was chosen in order to fit the lead silicate glasses.

Gels obtained starting from TEOS by sol-gel method have pores of almost 7 nm as was reported in literature [29]. The dust and bacteria from atmosphere have sizes >200 nm [30,31]. So, the gel applied on glass surface is protective against biofilm and dust, also. In case of studied samples a second film can be deposited to decrease the porosity and the effect is probably the same as impregnation used in literature by other authors [32–34].

2.3. Chemical resistance tests

The studied samples, coated and uncoated, were investigated under water attack during resistance tests according with standard ISO 598/1-71. After resistance tests they were dried in air.

2.4. Initial samples characterization

The vitreous state of initial samples has been evidenced by XRD and FT-IR measurements published in a previous paper [26].

The morphology and elemental analysis of initial samples were investigated by scanning electron microscopy (SEM) using a microscope, Quanta FEI 200 model, at an accelerating voltage of 10 kV, with an Energy Dispersive X-ray analysis detector. Sample preparation was minimal and consisted in immobilizing the samples on a double-sided carbon tape, with no coating.

The surface of initial glasses and after water resistance tests were investigated by X-ray Photoelectron Spectroscopy (XPS) with Quantera SXM equipment. The X-ray source was Al Kα radiation (1486.6 eV, monochromatized) and the overall energy resolution is estimated at 0.65 eV by the full width at half maximum (FWHM) of the Au4f7/2 line. In order to take into account the charging effect on the measured binding energies (BEs) the spectra were calibrated using the C1s line (BE = 284.8 eV, C/C (CH)n bondings) of the adsorbed hydrocarbon on the sample surface.

The elements extracted in water from initial and coated glasses during the resistance tests were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). ICP-OES 725 model, Agilent Technologies with radially-viewed plasma and a sealed CCD detector that requires no purging, a compact optical system, and an efficient RF system that sustains analytical plasma at lower argon flows was used for measurements. Image Mapping Technology (I-MAP) ensures complete coverage of all wavelengths by arranging 70,000 pixels in an uninterrupted array that exactly matches the two-dimensional echelle optical image. This ensures complete wavelength coverage from 167 to 785 nm and eliminates the need for separate sequential measurements. ICP-OES can determine up to 73 elements from The Periodic Table of the Elements.

3. Results and discussions

3.1. Morphological and chemical characterization of initial glasses

The initial glasses with compositions close to historical glasses were characterized by SEM and EDAX methods. In Fig. 1 the SEM images for initial glasses are presented. Glass 1 has uniform aspect where the light and heavy ions are distributed on all the surface. In the Glass 2, Glass 3 and Glass 4 where transitional metals were added the small darker regions can be distinguished.

In Table 3 the elemental compositions on surface established by EDAX are presented. As can be seen EDAX analysis detected Si, O and Pb atoms on all glass surfaces; other elements were below detection limits. The results show that transitional ions are bonded into glass network at a depth more than 100 nm and with a good distribution of elements on the surface of glasses.

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