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PROTECTIVE COATINGS FOR THE SILICATE GLASSES CONTAINING Fe_2O_3

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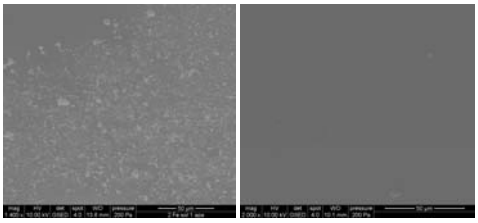
In the last years the interest to maintain historical objects in good conditions has increased. Most of the historical glass objects have the composition of alkali-silicate or lead silicate. The historical objects from glass contain also small quantities of oxides of transitional elements as Cr, Cu, Ag, Mn, Fe, etc. These small quantities (below 5% wt) of transitional elements determine the color of the glass objects but influence also the resistance of glasses at weathering. Previous investigations show that sol–gel silica coating does not change the appearance of artistic glasses when it is deposited on their surface. In this paper we studied two model glasses with similar composition as bracelet discovered in Romanian archeological sites. To hinder the phenomenon of weathering of historical glasses, the present work proposes the application of a silica sol–gel thin film on surface of model glasses containing transitional elements (Fe and Mn) and to investigate their chemical resistance in water.



INTRODUCTION

Most of the historical glass objects from Antiquity and Middle Ages have the chemical composition based of alkali-silicate[1-12] or lead silicate glasses.[13-16] In the last years the interest to maintain historical objects in good conditions has increased. The historical objects of glass contain small quantities of oxides of transitional elements as Cr, Cu, Ag, Mn, Fe, etc. All transitional elements act as modifiers of glass network and some of them increase the risk of deterioration.

Some authors described the effect of water attack on alkali-silicate glass surface that implies the reactions discussed below.[17-19]

An exchange between alkali atom from glass and hydrogen atom from water takes place following the reaction (1):

$$(Si–O–M)\ glass + H_2O \rightarrow (Si–O–H)\ glass + M^+ + OH^-aq \quad (1)$$

where: M is a metallic cation ($^{1+}$).

The glass surface is impoverished by alkali ions extraction and the $Si\text{-}O^-$ can form a silica film. In the case of silica soda lime glasses, weathering causes a general increase of the pH at the surface of the glass leading to the production of NaOH and a degradation of the structure, with the formation of voids in the areas where substitution of sodium by hydrogen occurs.

When the glass surface is in contact with an aqueous acidic medium for long time, the H^+ ions

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of the medium can replace the earth-alkaline or M^{2+} atoms in the glass:

$$Si–O–M–O—Si + 2H^+ \rightarrow 2(Si–O–H) + M^{2+} \quad (2)$$

where: M is metallic cation ($^{2+}$).

In fact, previous investigations[9, 14, 17] show that silica coatings do not change the appearance of artistic glasses when it was deposited on their surface. To hinder the phenomenon of weathering of historical glasses, the present work proposes the application of a silica sol–gel thin film on surface of model glasses containing oxides of transitional elements (Fe_2O_3 and MnO) that reproduced the bracelet from archeological sites discovered in Romania and tests their surface before and after coating.

Eight fragments of glass bracelets from the XVIII-XIX-th centuries discovered in Bucharest and thirty fragments of glass from Nufăru (Brăila) were analyzed by Bugoi *et al.*[1,2] The investigated objects had different glass recipes, indicating their manufacturing in several workshops.[1] The determined glass recipes turned out to be very different: some of the glass fragments are of soda-lime type (Stavropoleos church), other were of potash-lime type (Colței Street and General Florescu Street), while the fragments from Udricani Church and Cărămidarii de Jos Church belong to some mixed-alkali types of glass (soda-potash and potash-soda, respectively).[1]

Taking into account the long period of time during which the investigated bracelets fragments were buried in humid soil (hundreds of years), a layer of corrosion products had been formed on the bracelet surfaces (roughly estimated to several tens of μm).[1]

The chemical compositions of glasses bracelet discovered in Roumanian archeological sites are presented in Table 1.

EXPERIMENTAL

1. Glass preparation

The samples that reproduced historical glasses were prepared by traditional melt quenching route. Raw materials used in present work were: SiO_2, Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, Al_2O_3, $MnCO_3$ and Fe_2O_3 (Merck). The melting of the mixture of the raw materials in appropriate compositions was proceeded in an alumina crucible, into electrical oven at 1400°C, for 1h. The glasses were cast in carbon mould and thermally treated at 500ºC for 2h. Chemical compositions of the studied glasses are presented in Table 2.

2. Sol-gel silica coatings

The covering solutions have been prepared using TEOS (tetraethyl ortosilicate) [$Si(OC_2H_5)_4$] as sol-gel precursor, ethanol as solvent, distillated water for hydrolysis and HCl as a catalyst. Based on literature data[13,14,20] a solution with following molar ratio: C_2H_5OH : TEOS : H_2O : HCl = 10 : 1 : 3 : 0.03 was prepared.

The glass samples of dimension 2x2 cm were cleaned with detergent solution and distilled water, followed by distilled water and ethanol in ultrasonic bath for 3 minutes.

Table 1

Chemical compositions of glasses discovered in Romanian archeological sites[1,2]

Principal compounds (wt%)		**Traces (ppm)**	
Oxides	Chemical composition	Oxides	Chemical composition
SiO_2	61.2 – 70.3	P_2O_5	818 – 5692
CaO	7.2 – 9.8	PbO	94 – 4823
Na_2O	15.2 – 18.3	CuO	63 – 3127
MgO	1.1 – 4	ZnO	19 – 1308
Al_2O_3	1.2 – 2.5	CoO	139 – 878
K_2O	0.7 – 2.6	TiO_2	625 – 2780
Fe_2O_3	0.6 – 2.7	SrO	253 – 1171
MnO	0.4 – 3.7	SnO_2	128 – 682

Table 2

Oxide compositions of obtained glasses and their aspect and color

Glass	Chemical composition (wt%)								Observations
	SiO_2	CaO	Na_2O	MgO	K_2O	Al_2O_3	Fe_2O_3	MnO	
AG1	65	9	16	3	4	2	1	-	Transparent and Green
AG2	64	9	16	3	4	2	1	1	Transparent and Dark yellow

The protective silica coating was deposed on glasses by deep coating, with a withdraw rate of 50 mm/min and a dipping time of 60 s. Each sample was only half coated with the sol–gel film, so the reference was the half of sample without film. After deposition, the samples were dried in air at room temperature.

3. Tests of resistance at water attack

The studied glasses, coated and uncoated, were subjected to chemical stability tests. They were boiled in water at 98ºC for 1 hour according to the tests used to determine the glass resistance in water recommended by the ISO 598/1-71 standard. After test they were dried in air at room temperature and their surfaces were investigate by scanning electronic microscopy.

4. Samples characterization

The structure of obtained glasses was investigated by FT-IR Spectroscopy with a Nicolet 6700 apparatus in 400-4000 cm^{-1} domain; with sensibility of 4 cm^{-1}. The powders obtained from glasses were mixed with KBr and pressed in transparent pellets.

The XRD patterns on glass powders were collected by means of a Rigaku diffractometer type Ultima IV in parallel-beam geometry. The X-ray comes from a Cu tube (λ=0.15418 nm) operating at 40 kV and 30 mA. Counts were collected from 10 to 70 degree with a step size of 0.02 degree and a speed of 5degree/min.

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

RESULTS

1. Glasses characterization

The structure of prepared soda-lime glasses was investigated by X-ray diffraction and infrared spectroscopy. Fig. 1 shows the X-ray diffraction patterns recorded on the powders obtained by grinding of the obtained glasses, up to a grain size below 0,3 μ. The shape of XRD patterns was characteristic to vitreous state in glasses. The absence of peaks demonstrates that glasses are homogeneous, without micro-crystallites that prove its good quality.

The infrared spectra of studied glasses showed similar vibration bands but with some displacement of their positions, as can be noticed in the Fig. 2. All the bands are assigned to Si-O bonds in SiO_4 tetrahedra.

Depending on the structural level of characterization, glasses are constituted from structural entities with different stereo-chemical complexity degree.[21]

The structure of silicate glass consists in SiO_4 tetrahedra bonded in chains or network. The silica network can be considered as chains of tetrahedra bonded together. Due to this behavior the glasses can be considered also as polymerized structure. When metallic ions are added to silicate glasses they act as modifiers and depolymerize silica network. The result of their actions is the presence of isolated tetrahedra and pairs of tetrahedra in glass structure depending on the metallic ions quantity. Infrared spectroscopy is a technique that can identify the isolated tetrahedra and chains of tetrahedra, because any of them has characteristic vibrations that appear in spectra at different wavenumbers.

In the domain 650-770 cm^{-1} there is just one band that means the absence of the order at long distance as well as the absence of micro-crystallites. In the crystalline SiO_2 as coesite or stishovite there are 2-4 bands in this region of the infrared spectra.[22]

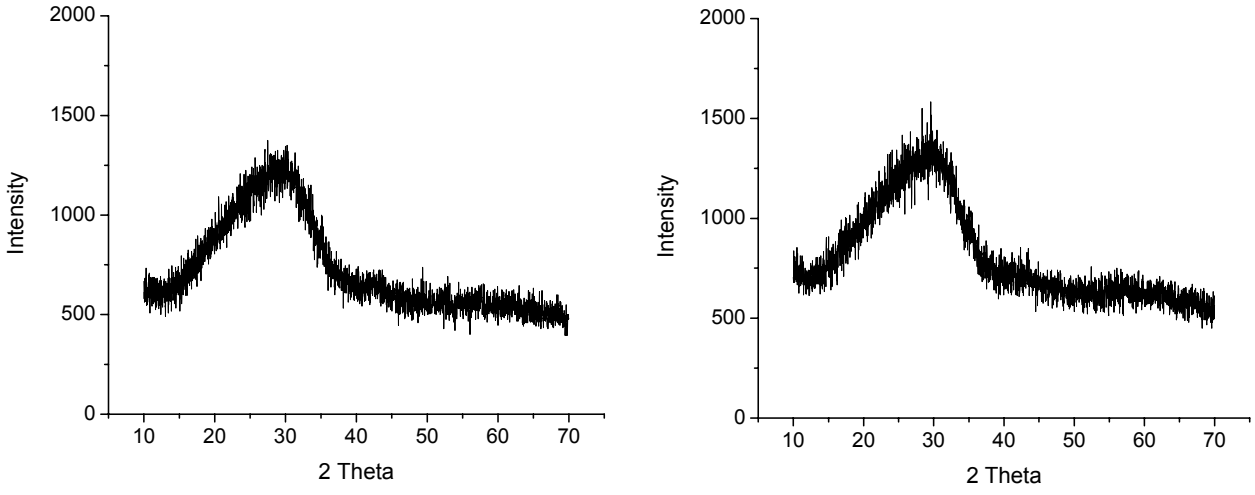


Fig. 1 – XRD patterns of the glasses: a) AG1, 2) AG2.

The broad band in 800-1500 cm^{-1} range is cleaved in two bands: one at 1083 cm^{-1} characteristic to chains of tetrahedra and the second band at 961/965 cm^{-1} characteristics to isolated tetrahedra. This behavior is due to the alkali atoms that depolymerize silica network.

FT-IR curve of AG2 glass that contains MnO besides Fe_2O_3 presents bands with lower intensity as compared to that registered in glass AG1. The band at 965 cm^{-1} is shifted to lower wavenumber due to the existence of a higher number of isolated tetrahedra and an increased depolymerization of structure. This phenomenon in AG2 glass is determined by the presence of MnO. The addition of MnO probably contributes to a change of iron oxidation number during the process of glass formation.[1,2]

2. Morphological characterization of coated and uncoated glasses after tests in water

Fig. 3 shows the SEM images of AG1 glass surface uncoated and coated with silica thin film after boiling in water for one hour at 98°C. In AG1 glass containing Fe_2O_3 white areas can be observed. The formation of Si-O-H bonds according to reactions (1) and (2) presented in introduction appears as white areas in SEM images. The results are in agreement with other research on the corrosion of historical glasses. Vilarigues *et al.*[11] reported for historical glasses in SiO_2-K_2O binary system an increasing corrosion rate when transition-metal ions as Cu, Fe and Mn are added to the glass. The glass with 1% Fe was the most attacked by water, followed by glasses with Cu and Mn.[11]

In silica film coated glass just few small white areas were visible. After coating the number of white areas strongly decreased and the surface become more resistant at water attack.

Fig. 4 shows the SEM images of the surface AG2 glass uncoated and coated with silica thin film after boiling in water for one hour at 98°C. On the surface of AG2 glass few small craters were observed after the chemical attack. For the silica film coated AG2 glass no sign of chemical attack was visible. The presence of MnO in composition of AG2 glass leads to a better resistance at water attack. The addition of MnO in composition of AG2 glass improved the chemical stability probably due to changing of oxidation state of Fe. Bugoi reports the intentional addition of MnO in the historical glasses in order to oxidize Fe^{2+} to Fe^{3+} and to improve their chemical resistance.[1,2]

We can conclude from the behavior of glasses at water attack that AG1 glass is less stable. In the case of AG2 glass that contains both Fe_2O_3 and MnO the stability increased. Another conclusion can be drawn referring to the silica sol-gel coatings that protect both glasses against water attack.

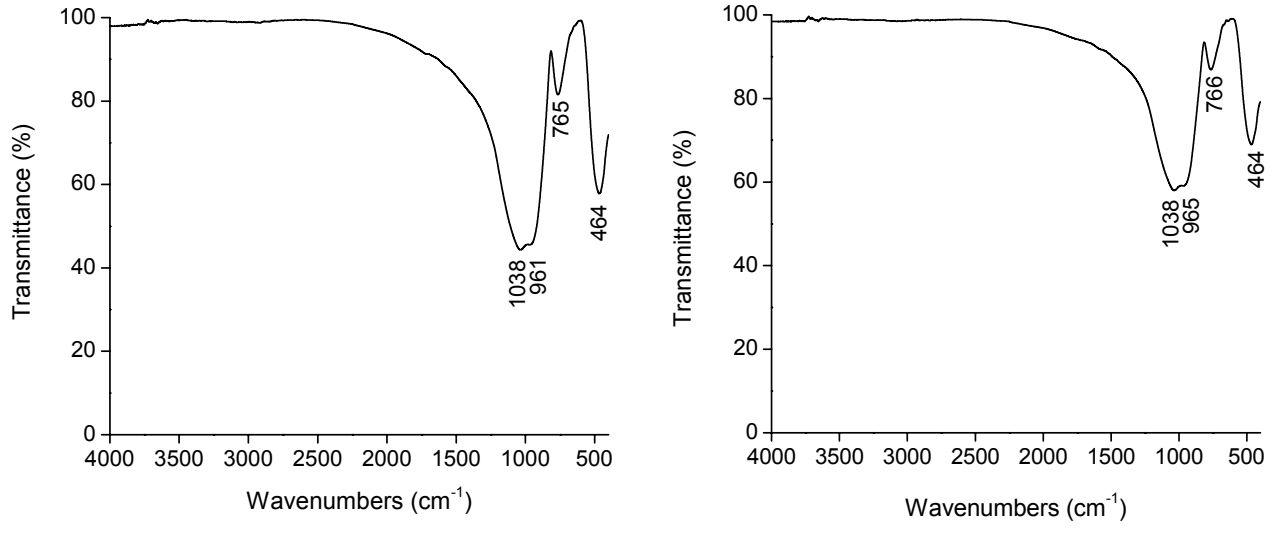
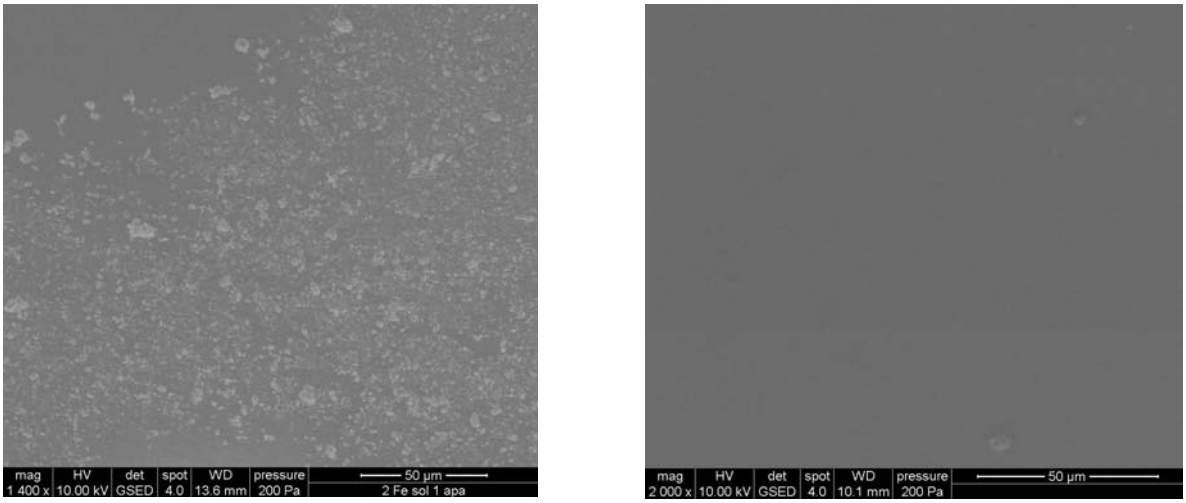
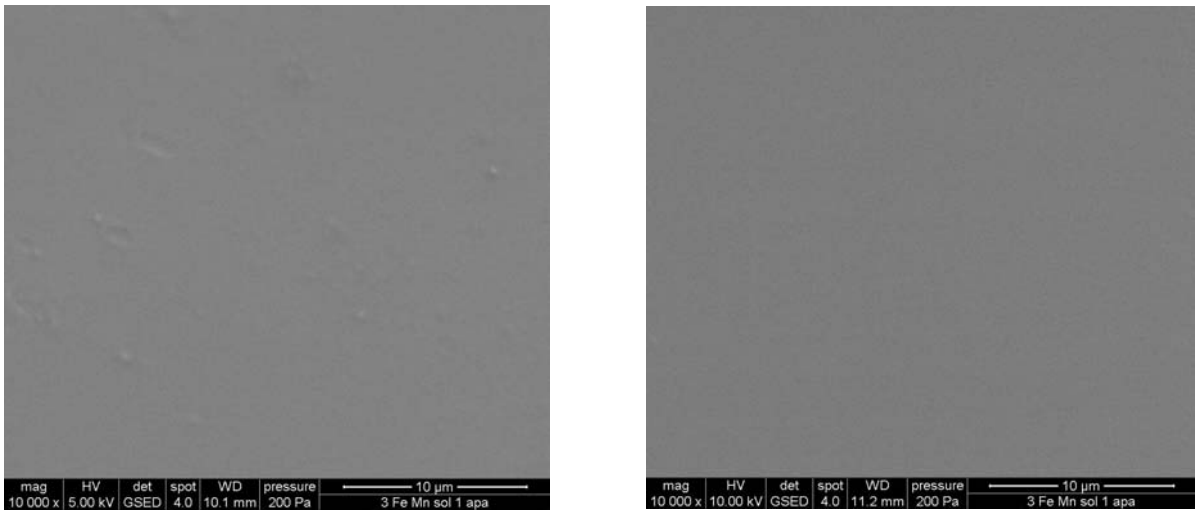


Fig. 2 –FTIR spectra of the glasses: a) AG1, 2) AG2.



a) b)

Fig. 3 – SEM images of AG1 glasses after resistance test in water:
a) uncoated glass; b) glass coated with sol-gel film.



a) b)

Fig. 4 – SEM images of AG2 glasses after resistance test in water:
a) uncoated glass; b) glass coated with sol-gel film.

CONCLUSIONS

Model glasses with similar composition of bracelet discovered in Romanian archeological sites were synthesized.

The XRD and FT-IR results show vitreous state of samples. The vibration bands in the FT-IR spectra are characteristic to Si-O-Si bonds.

The AG1 glass presents low resistance against water attack, the behavior being probably determined by Fe_2O_3 presence. The AG2 glass, which contains MnO besides Fe_2O_3, exhibits a better resistance against water attack even if the FT-IR spectra show an enhanced depolymerization of silica network.

The uncoated glasses exhibit white segregations or craves after water attack for 1 hour at 98˚C. The silica sol-gel coatings protect glasses against water attack as SEM images show. After the chemical test in water on the surface of the coated AG1 glass the number of defects strongly decreases.

The presence of MnO, besides Fe_2O_3, in AG2 glass improves the chemical stability against water attack.

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