



Sol–gel silica coating for potash–lime–silica stained glass: Applicability and protective effect



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ABSTRACT

The aim of this work is to test the applicability and the protective effect of a sol–gel silica coating on potash–lime–silica glasses of low durability. Such glasses were applied during the Romanesque and Gothic periods for manufacturing stained glass objects still in situ at historic buildings such as cathedrals or smaller churches north of the Alps. Their high potash content and low silica amount led to a low chemical stability and to degradation processes on the glass surfaces; a protection is hence necessary for the conservation of those art objects. Two synthetic glasses with compositions close to the historical stained glass were used for the studies. The sol–gel coating does not alter the optical characteristics of the surface and is compatible with the substrate since its composition and chemical–physical properties are similar to the glass it is applied on. Moreover, it can be easily applied and does not require any heating treatments after the application. It is therefore particularly suitable for the application on cultural heritage objects.

The effect of the sol–gel application was monitored and leaching tests with different times and pH values were performed both on coated and uncoated parts. The protective effect was verified using light microscopy and ToF–SIMS analyses were performed to check the ion migration (e.g. K, Na, Ca and Mg) and the interface between bulk glass and coating. The coating protects the glass from the formation of cracks also after severe treatments that would have caused serious damages on the uncoated glass.

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1. Introduction

It is predominant in the last century that glass has been exposed to an aggressive environment, due to the presence of pollution coming from industrial development, such as high amount of acidifying gasses in the air (NO_x , SO_2), causing acid rain with a pH value dangerous for sensitive glass such as potash–lime–silica glass, studied in this work. This kind of glass is characterised by a low amount of silica and a high content of network modifier ions (K and Na), introduced in the batch adding tree ash with the purpose of decreasing the melting temperature. This choice leads to a glass characterised by a better workability, with a lower melting temperature and an easier casting. On the other hand this kind of glass shows a lower chemical durability compared to glass with different composition such as soda–lime–silica glass, typical for the Mediterranean regions. This is due to the reaction occurring on the glass surface when it is in contact with water due to rain or to high levels of relative humidity: network modifier ions (K, Na, Ca and Mg) are replaced by hydrogen (H^+ or H bearing species such as H_3O^+) from solution [1–18].

The progress of this reaction leads to the formation of a superficial leached layer with chemical and physical characteristics different from the bulk; moreover the formation of thick crusts (up to millimetres), crystals, pits and cracks change the interaction of light with the surface and cause changes in the aspect [19,20]. Several window panes of churches and cathedrals in Central and Northern Europe present nowadays critical conditions due to those mechanisms: Objects show a weathered surface, the original transparency is often lost and the glass painting is in part or completely lost due to flaking phenomena, the surface might appear opaque and sometimes iridescence effects also occur [13,21–23]. To avoid further degradation and changes and for an appropriate preservation of our cultural heritage, a treatment is therefore necessary.

Some techniques have already been used such as a passive protection of the glass objects with an outdoor glazing system positioned in front of the stained glass window to preserve it from mechanical and atmospheric damages. Other methods consist on the application of consolidants (i.e. PVA) and chemical inhibitors [24–28] directly on the surface of the glass after an adequate treatment [29,30]. In general a good protecting coating should meet some conservation requirements (preservation of the original aspect of the objects and their optical characteristics) and improve certain properties (resistance to aggressive environments, slow down the rate of degradation processes) [31]. In the

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Table 1
Chemical composition of glass M1 and M3 expressed in wt.% (mol% in brackets).

	SiO ₂	K ₂ O	CaO	MgO	Na ₂ O	Al ₂ O ₃	P ₂ O ₅
Glass M1	48.00 (53.16)	25.50 (18.01)	15.00 (17.80)	3.00 (4.95)	3.00 (3.22)	1.50 (0.98)	4.00 (1.88)
Glass M3	60.00 (62.27)	15.00 (9.93)	25.00 (27.80)	–	–	–	–

past the organic coatings were commonly applied, e.g. with Paraloid B72 (acrylic resin); in general, such coatings show some disadvantages such as lower scratch and abrasion resistance, the tendency to yellow under external exposure and to change their characteristics such as the solubility, making them hardly removable from the objects when further restoration treatments are necessary; moreover the porous structure tend to incorporate dust causing an opaque appearance. Due to those problems coating based on the sol–gel technique were developed [32–41].

In our work a pure silica sol–gel coating was tested, counting on the high compatibility with the substrate and the final resistance of the layer due to the absence of organic components, avoiding any problems of colour change and chemical instability [34,35,38,39].

A silica alcoholic suspension based on sol–gel technology (SIOX-5) was used to obtain a highly pure silica protective film [36]. An important aspect of this formulation is that the formation of the glass layer doesn't require any thermal treatments in contrast with other experiments where densification temperatures up to 250 and 400 °C were tested [37,42] and it can be easily applied by spray and dip coating methods.

The problems faced during the studies were the possibility of ion migration from the bulk to the sol–gel layer during the application of the coating: Previous studies [34] have shown that lead glass is not suitable for this kind of treatments since during the application a consistent ion migration occurred causing colour changes and final opalescent effects. Therefore, the possibility of application of the sol–gel silica coating was tested on potash lime silica glass and further resistance tests to an aggressive treatment were performed, comparing the results with previous experiments done on untreated samples.

2. Experimental

Glass samples of two different compositions typical for mediaeval stained glass were prepared, accurately polished and partially dip-coated. The samples were characterised using optical microscopy and ToF–SIMS measurements were performed with the aim to study the interface between the bulk glass and the coating, focusing in particular on the ion migration [43,44]. Afterwards the samples were aged simulating an aggressive treatment in acidic solutions and analysed afterwards to check the resistance of the coating to the leaching effect.



Fig. 1. Glass M1. The lower part is coated with sol–gel silica coating (sample size 8 × 30 mm²).

2.1. Sample preparation

The glass samples were prepared starting from glass bars and polished using SiC paper up to 4000 mesh. The details of the preparation methods are already described in literature [45] and the compositions of the two glasses are reported in Table 1:

The sol–gel (SIOX-5) was prepared by Siltea S.r.l. with tetraethoxysilane (TEOS) as a silica precursor. The pH of the solution is 4–5. For catalyst and molar ratios see Ref. [38].

The film was applied by dip-coating with a drawing rate of 10 cm · min⁻¹. Samples were dried at room temperature without any heating treatment for several days before the analysis.

2.2. Analysis techniques

To F–SIMS measurements were performed with TOF–SIMS⁵ (ION TOF GmbH, Münster, Germany) using an alternated sputtering for sample erosion and for sample measurement (interlaced mode) using a bismuth liquid metal ion gun (LMIG, Bi⁺, 25 keV) in positive detection with a High Current Bunched Mode, enabling high mass resolution (10,000). Sputtering was performed with a raster size of 300 × 300 μm² using O₂⁺ (1 keV, ~200 nA).

The Field of View used was 100 × 100 μm² and the sampling was 128 × 128 pixels.

Sputtering time and pause time between sputtering and the following analysis were established depending on the sample; to compensate the charge an electron flood gun (20 V) was used for up to 3 s between the sputtering and the analysis [46]. Using this expedient it was not necessary to coat the samples with a conductive layer (such as gold or carbon) and consecutive leaching on the same sample could be performed.

After the measurements the samples were coated with a thin gold layer (~50 nm) and crater depths were measured using a Digital Holographic microscope (DHM, Lyncee Tec, Switzerland) in order to calibrate the depth scale.

2.3. Experimental procedure

After the characterisation of the coating, different leaching experiments were performed: The coated samples were kept for different times in hydrochloric, sulphuric and nitric solutions (prepared from Titrisol® of Merck, Germany) at room temperature, stirred with a Teflon coated magnetic stirrer and keeping the pH constant.

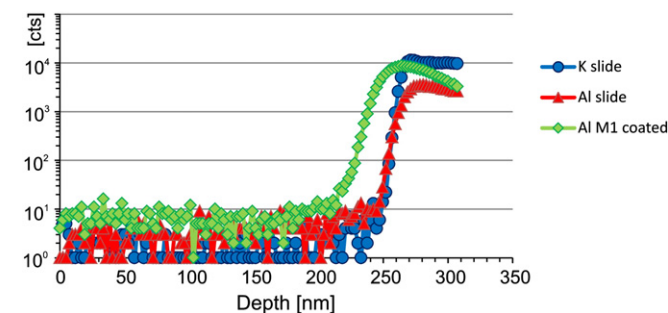


Fig. 2. ToF–SIMS depth profile of Al and K signal of a coated microscope slide and coated glass M1.

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