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Application of atomic force microscopy to the study of glass decay

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Abstract

Conventional methods such as scanning electron microscopy with energy dispersive X-ray spectrometry are commonly used to characterize corroded glasses. However, their use is often restricted when glass pieces come from historical artworks and may not be damaged. Atomic force microscopy can be an alternative method for characterizing such glasses since it is an essentially non-destructive technique which allows their topographic analysis with good vertical and lateral resolutions. In addition, samples do not require any previous manipulation. The application of atomic force microscopy to study glass decay is reported in this paper. The main goals of the research were to study the corroded texture of both historical glass pieces and model glasses weathered in the laboratory, and to determine and compare the chemical corrosion mechanisms which occurred in both cases. The resulting data suggest that atomic force microscopy can be a useful technique for characterizing decay mechanisms in historical glasses.

Keywords: Glass; Decay; Microscopy; Weathering; Chemical resistance

1. Introduction

Corroded glasses usually present a delicate surface with abundant craters and pits frequently filled with products of an ion-exchange which form crusts of variable thickness and density [1]. Such glasses are commonly analyzed by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) [2]. However, the study of corroded glasses through these techniques is often a difficult task, especially when samples come from historical stained glass windows or some other kind glass artwork from the cultural heritage, since they have to be preserved and cannot be destroyed or damaged. In addition, grisailles and other decorative superficial

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glazes and paints also pose serious difficulties since they are formed by glassy materials as well and, consequently, with the same microstructural features as those of the underlaying glass artwork. In light of this situation, it is clear that new characterization methods are needed [3,4].

Atomic force microscopy (AFM) may be a suitable alternative method for characterizing historical corroded glasses. AFM is an essentially non-destructive technique which allows the performance of topographic and textural analyses with good resolution (0.01 nm vertical and a few nanometers lateral) [5–7]. Besides, it presents the advantage that the samples to be observed do not require previous manipulation and do not have to be submitted to vacuum, thereby avoiding any kind of alteration on either the delicate surface or the corrosion crusts present on historical glasses. Although there are AFM instruments that can analyze the surfaces of large samples most instruments do in fact require relatively small samples, similar to those ones that would fit in an SEM specimen stage.

Medieval stained glass windows were commonly produced from potash–lime–silica glasses [8]. As is known [9], these glasses are very sensitive to weathering conditions, especially against humidity and atmospheric pollutants. Acid pollutants such as SO_2 and NO_x combined with a high relative humidity produce the phenomenon of acid rain. Under such aggressive environment, Medieval stained glasses experience a strong chemical attack which causes the leaching of alkaline ions, the formation of a superficial silica gel layer, the precipitation of insoluble salts as a result of the corrosion mechanism and, finally, the formation of interconnected craters and pits [10]. Under these environmental conditions, historical glasses lose mass, transparency, original colourings and brightness. In turn, grisailles and other glassy paints can be detached and then the aesthetic and iconographic value of the stained glass windows decreases dramatically.

Prior to the start of any kind of restoration or preservation work, knowledge of either the current state of conservation or the degree of corrosion of the glass pieces which form part of the historical stained glass windows is a key factor. Cleaning and repairing tasks depend on the kind of attack experienced by the glass and these attacks need to be investigated on the glass surface. In this regard, AFM arises as a non-conventional observation technique for delicate materials and can play an important role in the characterization of corroded surfaces from historical glasses, as well as in the study of glasses subjected to accelerated weathering processes. Comparison of the topography and morphology of artificially weathered model glasses and original historical pieces may enable the assignment and understanding of general chemical decay phenomena in glasses. Thus, the goals of the present work were, on the one hand, to study the corroded texture of both historical glass pieces and model glasses intentionally weathered in the laboratory by means of AFM. On the other hand, it was also aimed at assigning the chemical corrosion mechanisms experienced by the historical glasses from those produced in model glasses under controlled laboratory conditions.

2. Experimental

Corroded glass pieces from a historical stained glass window panel of the Cathedral of León (Spain, 13th century A.D.) and a model glass with similar composition prepared in the laboratory were studied. The model glass was melted in an electric furnace at about 1400 °C for 2.5 h, starting from Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, $AlPO_4$ and $MnCO_3$ pure chemical reagents. Washed quartz sand (99.5 wt.% of SiO_2) was the source for silica. After casting in a brass mould and hand pressing, plates of $1.5 \times 2.5 \times 0.4$ cm in size were obtained. These samples were annealed at 650 °C to avoid mechanical stresses and cracking.

Several samples of the model glass were artificially weathered following two different patterns:

a) under a humid SO_2 atmosphere in a Kesternich chamber for 25 time cycles. In each cycle 50 ppm of SO_2 were added. Each time cycle lasted 8 h and was carried out at 40 °C under a 100% relative humidity. After each cycle the chamber was opened and the SO_2 atmosphere was slowly exhausted during 16 h up to reach room conditions.
b) under an alkaline attack in liquid medium, undertaken by dipping the samples into a 2 M NaOH solution for 6 h at room temperature. After that, the glass samples were withdrawn from the solutions,