Atomic Force Microscopy study on surface of Thai decorative glasses

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In this work, Atomic Force Microscopy (AFM) was used to study atomic density on the surface of the decorative glasses found in Thailand. Scanning electron microscope coupled with energy-dispersive X-ray fluorescence analysis system (SEM-EDS) was also carried out to characterize their surface morphology and composition. Microstructure and nanostructure, roughness and topology of the ancient Thai decorative glass samples have been compared with those of the modern glass which imported from foreign country and the new-constructed decorative glass that fabricated by conventional melting based on local resources. It was found that the weathering and the different physical and chemical degradation led to the alteration of the glass surface. The resulting data suggested that AFM corporated with SEM-EDS can be useful techniques for characterizing the surface of the glassy materials.

Keywords AFM; SEM-EDS; Thai decorative glass

1. Introduction

Glass has been played an important role as a pragmatic and esthetic item in all period of history; hence the investigation of its chemical durability has been a key issue in glass conservation and restoration studies. It was known that the stability of glass against natural environments was a very complex process that depended both on the characteristic of the glasses (composition, surface roughness, etc.) and external conditions (time, temperature, climate, etc.) [1-4].

Historical glasses have been found and used in ornaments and decorations in Thailand for several hundred years as seen by archaeological evidences which discovered in regions throughout the country. Decorative glasses can generally be found as architectural components in places, such as, ancient palaces and Buddhist temples which have been center points among Thai commoners for centuries. Ancient glasses are classified into two categories: Ancient Thai Glass (ATG) found mostly in the central region of Thailand and Ancient China Glass or Ancient Burmese Glass (ACG/ABG) is widely used in conventional Lanna-styled architectures in northern Thailand. Glasses of various colors ranging from transparent to blue, green, red, and amber have been found. Under the tropical sun, it gives out an artistic harmony of flamboyance and serenity [5-7]. Previous analyses [8-14] of the ATG and ACG/ABG using X-ray fluorescence spectroscopy showed silica and lead oxide being as major compositions. Transition elements, such as, Fe, Cu, Co and Au, were found in the glass matrices as colorants. As the glasses have kept deteriorating over time, restorations must be performed routinely to preserve these cultural crafts for later generations to appreciate. However, presently there are no glassmakers producing this type of glasses. Only modern, imported, difficult-to-cut glasses (MIG) with greater thickness and shorter lifetime are available in the market. The new-constructed glass (NCG) was fabricated with the same composition as the ATG.

Previous studies showed that SEM was a one of conventional methods which commonly used to characterize the glass corrosion for a long time. AFM was also a non-destructive and non-invasive direct technique that obtained the performance of topographic and texture analysis without submitting to vacuum [1-4, 15-18].

2. Materials and methods

The four blue-colored decorative glass samples from different times and provenance consisted of B-ATG, B-ACG/ABG, B-MIG and B-NCG which were all flat and about 0.2 cm thick were used to characterize in this study, as shown in Fig. 1. The B-ATG and B-ACG/ABG were broken with deterioration over time and fell down to the ground. The B-ATG sample was decorated on the stucco at the Temple of the Emerald Buddha in the Grand Palace (Bangkok) which was constructed in 1782 A.D., whereas the B-ACG/ABG sample was decorated on the gable of the Viharn at Wat Ket Karam (Chiang Mai) around 1438 A.D. The third one, the B-MIG was bought from market on 1996 A.D. The last one, the B-NCG was fabricated on 1997 A.D.

Structure and composition were carried out using a Jeol JSM 5410 LV SEM coupled with a Oxford Instruments INCA Penta FETx3 analytical system. No sample preparation on the glass surface was possible. For each sample, three X-ray fluorescence spectra were taken at different positions of the sample using a voltage of 15 kV, an elapsed live time of 60 s. The chemical compositions were conventionally determined in oxide weight percent.

AFM measurements were carried out using an Asylum MFP-3D microscope. They are observed in intermittent contact mode or tapping mode. The image acquisition is realized by controlling the deflection. They are constructed by

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scanning the surface with speed at 2.0 Hz, in the 1x1 micron of scan area and 100 nm in Z scale. In order to measure correctly, the AFM must be placed in homogeneous environment and free pollution.

3. Results and discussion

Table 1 showed the compositional analysis of the B-ACG/ABG, B-ATG, B-MIG and B-NCG samples using EDS. The XRF data indicated that sodium-potassium lime silicate glass, with and without lead oxide was used as glass base for manufacturing ACG/ABG and ATG, and MIG, respectively. The main components were SiO$_2$, and Na$_2$O for MIG and PbO for ATG and ACG/ABG. It was shown that SiO$_2$ and Na$_2$O contained in MIG were higher that those of ACG/ABG and ATG. The transition metals were found to be MnO, Fe$_2$O$_3$, CoO. CuO was only presented in the MIG. It was proved that Co ion was mainly affected on the blue coloration. As well as, a small amount of As$_2$O$_3$ probably used in the glass refining process was also detected.

SEM micrographs showed a variable amount and distribution of porous and an earthy-like deposit or crust can be observed on some areas of the glass surface, Fig. 2.

| Table 1 Chemical analysis of Thai decorative glass using EDS |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Na$_2$O | MgO | Al$_2$O$_3$ | SiO$_2$ | K$_2$O | CaO | MnO | Fe$_2$O$_3$ | CoO | CuO | As$_2$O$_3$ | PbO |
| B-ACG/ABG       | 4.56    | 0.30 | 4.01 | 62.92 | 1.86 | 5.98 | 0.66 | 1.94 | nd | 0.81 | 16.43 |
| B-ATG           | 6.88    | 0.39 | 3.85 | 52.86 | 6.99 | 3.89 | 0.34 | 1.52 | 0.20 | nd | 0.17 | 22.93 |
| B-MIG           | 16.86   | 0.32 | 2.71 | 72.11 | 1.24 | 2.88 | 0.25 | 1.16 | 0.44 | 0.31 | 0.67 | 1.38  |
| B-NCG           | 5.59    | 0.42 | 2.19 | 53.80 | 7.84 | 4.56 | 0.63 | 1.60 | 0.23 | nd | 0.10 | 23.64 |

AFM images in Fig. 3 showed an extremely rough surface for the glass samples with different topography. It was shown that more corroded areas presented on the surface of the B-ACG/ABG and the B-ATG than those of the B-MIG and B-NCG. It was also shown that by comparison within the proximate time, the surface of the B-MIG had more crater-shaped pits than that of the B-NCG.

Considering of the compositions, it was found that the higher the concentration of network-modifying alkaline oxides such as Na$_2$O and K$_2$O, the more the influence of chemical attack on glasses, and the higher the concentration of main network-forming oxides such as SiO$_2$, PbO and Al$_2$O$_3$, the more the chemical stability of glasses.

Fig. 1 Thai decorative glass

Fig. 2 Microstructure of Thai decorative glasses using SEM

Since the composition of the glasses was mostly very heterogeneous, AFM should be coupled and complemented with other non-destructive microanalysis system such as PIXE (particle induced x-ray emission spectroscopy) and SRXRF (synchrotron radiation induced x-ray fluorescence spectroscopy) in order to obtain more corrected results.

4. Conclusion

The morphological, chemical and micro-textural characterization of the decoration glass samples found in Thailand allowed describing the corrosion process naturally by weathering. The gathered information in this work has been of great related with stability against weathering. It led to find out the protection system that will be very effective to protect these glasses against future environmental aggressiveness.
It can be concluded that the corrosion of glasses can be easily observed by means of AFM. The obtained AFM topographic images could be used as reference microstructures for the further identification and diagnosis of decay signs and chemical damage on glasses.

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