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Redox profile of the glass surface

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ABSTRACT

The redox profiles of tin, iron and sulfur at the float glass surface were determined on purposely cut samples by Electron Probe Micro Analysis (EPMA), X-ray Fluorescence mapping and X-ray Absorption Spectroscopy (XAS) at the micron scale. Going inward from the surface to the bulk, it was observed that (features do not depend on the glass thickness (holding time) though they extend over depths that vary from ca. 25 to 50 μm): (i) after a diffusion-driven decrease and prior to vanishing, the tin concentration passes through a local maximum (the tin hump), where stannous ions, which dominate the shallow layers, switch to stannic ions; (ii) the iron concentration decreases, passes through a minimum at the tin hump where iron is in the more reduced form (lowest Fe^{3+}/Fe^{2+} ratio); it then increases and, after a hump which appears as a chemical echo of the tin hump, it reaches the bulk value; (iii) the concentration of sulfur increases up to reach the bulk concentration beyond the tin hump region. In a mixed S^{6+}/S^{2-} form at the surface, sulfur is only in sulfate form in the bulk.

In the case under study, the iron concentration is much too low to balance the redox reaction $Sn^{2+} \rightarrow Sn^{4+}$ that occurs at the tin hump. Sulfur is shown to play the role usually attributed to iron, according to the reaction

$$4Sn^{2+} + S^{6+} \rightarrow 4Sn^{4+} + S^{2-}$$

The occurrence of that reaction is supported by the appearance of sulfide S^{2-} in the tin hump region with an appropriate concentration profile of a much stronger S^{2-}/S^{6+} ratio on the tin side than on the atmosphere side of the float glass. The conclusions drawn herein likely apply to the many cases in which the glass composition is similar as that encountered herein.

1. Introduction

The first step of the float process consists in spreading the glass melt onto liquid tin to take advantage of the balance between surface and interface tensions to produce flat glass sheets. Those conditions, that are quite suitable to produce glazings for common use, are not adapted regarding new applications which raise the level of demand required for the production of float glass, such as the manufacture of supports for electronic display elements that needs nearly atomically smooth substrates [1] and the control of the nanomechanical properties of glass surfaces [2,3].

The control at the microscopic level of the glass surface requires a detailed understanding of the redox reactions involved in the float process. The two faces of the glass ribbon are different. To prevent the oxidation, the whole part of the process which involves the tin bath is run in reducing conditions by circulating a gas mixture comprising nitrogen and hydrogen. Due to such an environment, the chemical composition of the skin of float glass differs from that of bulk over a few tens of microns with different behaviors on the atmosphere side and on the tin side. Complex concentration profiles result from interdiffusion and redox reactions at the interface between tin and glass melt [1]. Researches focus on the concentrations and profile of iron species because that element is stressed to be central [1,3–6] in the formation of the tin satellite peak that appears at a depth of ~5–20 μm from the glass surface. The so-called tin hump was first identified by Sieger [3]. It has been then demonstrated by Mossbauer spectroscopy that the shallower part of the tin profile mostly involves Sn^{2+} ions and that the tin hump is dominated by Sn^{4+} ions [5,7,8]. On the basis of a simulation, Wang et al. suggest that the tin hump arises from an easy diffusion of Sn^{4+} [9]. At variance, Cook and Cooper [1] argue that the diffusion of stannic ions that act as glass modifiers is much easier than that of stannous ions that behave as glass formers. These authors and Frischat et al. [5,6] assign the occurrence of the tin hump to redox reactions. They assume that the formation of stannic ions within the

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glass is favored by the presence of ferric ions via an ion-exchange process:

$$Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+} \quad (1)$$

A maximum in iron concentration is also observed at the extent-end of the tin profile. It is associated to the inward diffusion of the then produced ferrous ions [1]. There is also some suggestion that the formation of Sn^{4+} could involve sulfur [10,4,5], although no evidence was ever provided.

To date, direct measurements of the redox profile of the glass surface are lacking. The objective of the present work is to determine concentration profiles of tin, sulfur and iron at the vicinity of a float glass surface by examining cuts of glass plates by microanalysis. Electron Probe Micro Analysis (EPMA) was used to determine quantitatively the concentration as a function of the depth. Micro X-ray Fluorescence mapping and X-ray Absorption micro-Spectroscopy (XAS) allowed a characterization of the oxidation states and their spatial distribution. These techniques have a comparable resolution of about 1 μm. Therefore, they were suited to analyze concentration along the profiles under study that extend over tens of microns. Moreover X-ray spectroscopy is of relevance to determine the chemical states of tin, sulfur and iron in glasses [11]. It has been chosen to work on common float samples with iron (Fe_2O_3) and sulfur (SO_3) bulk concentrations of 0.1 and 0.3 wt.%, respectively. It will appear during the discussion that this choice allows to pinpoint the respective contributions of these two species to the redox profile of the float glass surface.

2. Experimental

Samples were float glass plates with different thicknesses: 3, 4, 6 and 10 mm. Glass surfaces were analyzed by sampling both the bath side and the atmosphere side. In order to study concentration profiles, the bath sides of two glass plates were glued together (Fig. 1), and this cross-section sample was prepared by grinding with SiC abrasive papers and then polishing with diamond (3 and 1 μm size).

A quantitative analysis of the concentration was achieved on the 10 mm thick sample by a Cameca SX50 Electron Probe Micro Analyser employing four different wavelength-dispersive spectrometers, at Saint-Gobain Recherche. Such elemental analysis was realized on the bath surface and the bulk (from the cross section) after plating them with a thin graphite conducting layer. The experiments were performed with an accelerating voltage of 15 kV and a beam intensity of 10 or 150 nA according to the element. Five different spots were analyzed in every case. The composition of this glass studied here is shown in Table 1, together with that of the glass CNF 0.2 studied already by Farges et al. [12] (see below).

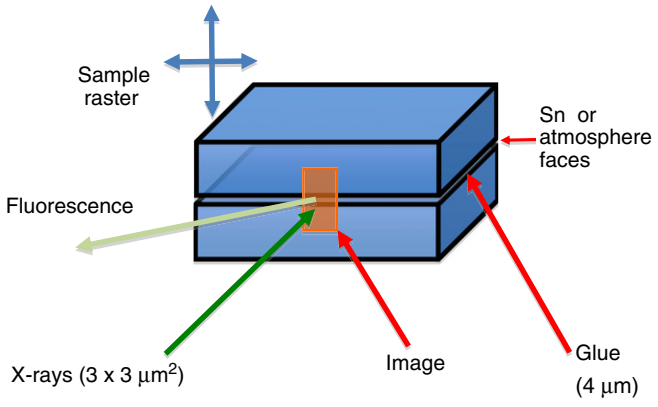

Fig. 1. Geometry of the experiments.

Table 1
Composition of the float glass used herein (weight per cent of oxides). Error bars are maximized by the last digit. Comparison with the CNF 0.2 composition analyzed by Farges et al. [12].

	SiO_2	Na_20	MgO	CaO	Al_2O_3	Fe_2O_3	SO_3
This work	71.9	14.0	3.9	8.7	0.7	0.09	0.26
CNF 0.2	72.1	13.8	–	13.9	–	0.2	–

X-ray experiments have been done at the LUCIA beamline [13], installed on the Swiss synchrotron facility SLS (Villigen). The monochromator is equipped with a pair of Si(111), and the spot size was set to $3 \times 3\ \mu m^2$ at all energies of interest. By using the two classical techniques of the total electron yield (TEY) and fluorescence yield (FY), we could probe two different depths into the sample, typically 0.5 μm in TEY and 5 μm by FY. The TEY signal is obtained by a measure of the sample drain current, while the FY is detected by a monoelement (10 mm^2) silicon drift diode.

The analysis of the oxydation state of the different elements was be done comparing the near edge spectra (XANES) to those of reference compounds whose valency is well known. XANES of sulfur in several well characterized compounds were purposely recorded. Tin spectra were compared with published data [14]. Finally, the oxydation state of iron was determined by an analysis of the pre-peaks [12,15,16] as explained below.

To avoid any artifact from the self-absorption of the fluorescence signal, the common surface of the glass was set horizontal, and this common surface could be precisely localized by examining the silicon mapping since this element was expected to exhibit a constant concentration throughout the sample (Fig. 1). Given the flux on the sample of about 5×10^{10} photons/s, we could be concerned by possible radiation damage or photoreduction processes, mostly on sulfur which is well known to be a very sensitive element. In order to check that, we did successive experiments on the same point. In the case of tin and iron, the spectra remains identical and therefore we believe that radiation damages should be of a minor importance in that case. At the contrary, and this will be discussed in Section 3.4, some of the sulfur features could be the result of the irradiation, as it has been also pointed out by Wilke et. al. [17].

3. Results

3.1. Mapping of the different elements

The concentration profiles at the surface of the 10 mm thick float glass plate were first examined by EPMA. Tin penetrates in the glass over a depth of ≈40 μm. Going inward, its concentration decreases steeply prior to show a buried peak — the so-called tin hump — at 10–20 μm below the surface. The concentration of iron is peaking at the extreme surface. Then, after a depleted zone with a minimum just before the tin hump, it increases to peak again as the Sn concentration vanishes, prior to reach its bulk value. The sulfur concentration, which is at its lowest level at the glass surface, increases progressively to level off at a depth of ≈15 μm which coincides with the Sn hump. Its bulk value is about three times higher than the surface value. Sn, Fe and S profiles that are observed herein are consistent with the commonly accepted picture [1,3]. Fig. 2 shows the images obtained on the 10 mm thick sample for the different elements analyzed in this study, with two Sn faces stuck together as described previously. The silicon and iron maps have been obtained with an incident energy of 7130 eV, the tin map has been made at 3990 eV in order to avoid the contribution of calcium present in the glass, and the sulfur one has been recorded at 2500 eV in order to maximize the fluorescence signal. On the silicon map, which must be uniform, we see the signature of the glue (blue and green zones) which amounts about