

DIFFUSION IN THE SURFACE LAYER OF FLOAT GLASS

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Surface interaction of Float glass with melts of potassium nitrate, silver nitrate and the mixture of copper sulphate and ochre was studied at 350 °C, 420 °C and 600 °C. The distribution of the ions in the surface layer indicates that the course of the interaction depends on tin content in the glass. This finding is significant with respect to surface treatment of Float glass by ion exchange, which will have a different course with the surface formed in contact with the tin bath, than with the opposite one.

INTRODUCTION

Compared to other commercial types of glass, the Float glass exhibits a different chemical composition of the surface layer. Owing to the technology of manufacture, there are also differences in the chemical composition of the two surface layers, above all based on a relatively high tin content in the surface layer that is in contact with molten tin during the manufacture.

There arises the question whether the tin concentrated in the surface layer [1] participates e.g. in the interaction of the glass with melts of the respective salts. The participation of tin can complicate considerably the currently accepted concept of a simple exchange diffusion mechanism based on the principle of exchange of foreign ions entering the glass for alkali ions originally present in the surface.

EXPERIMENTAL APPARATUS AND PROCEDURE

Description of the apparatus

The thermal exposure of the specimens was effected in a vertical tubular furnace (Fig. 1) provided with thyristor temperature control [2]. The vertical tubular furnace 1 was fixed in the stand of Brabec's furnace 2 with a pull-out bottom carrying corundum tube 3 with an alporite shaped block. The specimens were placed in a holder of aluminium sheet 6 where they were kept at a distance of approx. 3 mm. The holder was fixed by kanthal wire to a corundum capillary with Pt/PtRh7 thermocouple situated with its joint approximately at the specimen centre. A Fe/Co8 thermocouple was placed at the centre of the furnace heating zone and its ends were connected to the thyristor temperature controller working with an accuracy of ± 2 °C.

Experimental procedure

The experiments were carried out on commercially produced Float glass 4 mm in thickness. Its mean composition was 72.18 SiO₂, 0.85 Al₂O₃, 0.052 Fe₂O₃, 8.45 CaO, 3.86 MgO, 0.43 K₂O, 13.89 Na₂O, 0.28 SO₃ [wt. %]. Specimens with an area of approx. 2×10^{-3} m² were cut out of the sheet. Before the exposure proper, the

specimens were washed with distilled water, degreased in ethyl alcohol and dried.

The specimens were subjected to thermal exposure in KNO_3 melt, in molten mixture of $\text{AgNO}_3 + \text{KNO}_3$ (20 mol % AgNO_3) and after coating with a war-nishing mixture of $\text{CuSO}_4 + \text{ochre}$ (1 : 1). Different working procedures were used in the individual instances.

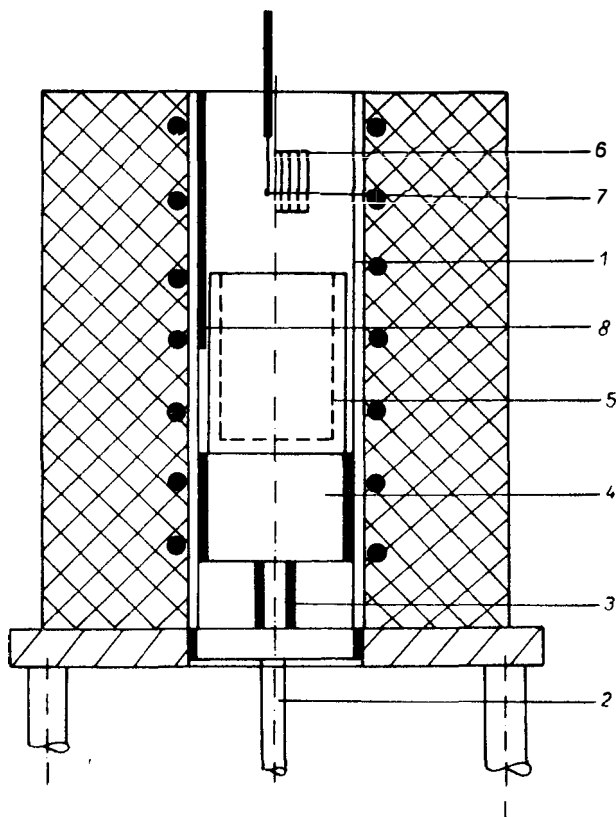


Fig. 1. Schematic diagram of the apparatus for thermal exposure. 1 — tubular furnace, 2 — stand of Brabec's furnace, 3 — Al_2O_3 tube, 4 — porous brick from Al_2O_3 , 5 — stainless steel crucible, 6 — Al sheet holder, 7 — thermoelectric couple Pt—PtRh, 8 — regulation thermoelectric couple Fe—Co

In the case of surface interaction with KNO_3 or AgNO_3 always three specimens were placed in the Al sheet holder. KNO_3 or the $\text{AgNO}_3 + \text{KNO}_3$ mixture (20 mol % AgNO_3) was introduced into a stainless steel crucible, this placed in the furnace and the furnace closed with a fibre corundum plug. On reaching the working temperature, the holder with the specimens was suspended from a kanthal wire in the furnace and then immersed in the melt. After the given time of exposure, the holder with the specimens was withdrawn from the melt and the specimens allowed to cool down to room temperature. After washing with hot water the specimens were rinsed with distilled water, ethanol and dried.

The KNO_3 melt temperature was chosen at 420°C and the exposure took 24 hours. In the $\text{AgNO}_3 + \text{KNO}_3$ mixture, the temperature and time of exposure were 350°C and 14 hours respectively.

A different procedure was used in treating the Float glass specimens with the CuSO_4 -ochre varnishing mixture. A mixture of anhydrous CuSO_4 with ochre (1 : 1) was first ground in an agate mortar and then diluted with distilled water. The paste was applied with a flat brush on the degreased surface so as to produce a uniform coating. The specimens were then dried freely in air to avoid cracking of the layer, and then in a drying oven at elevated temperature. A platinum sheet was placed on an alporite block on the furnace bottom, the furnace heated at 600°C , and the specimen then laid onto the sheet and kept there for 30 minutes. After this exposure, the specimen was gradually cooled down, the varnishing mixture removed with brush and water, and rinsed with distilled water and ethanol.

To determine the concentration distribution of Na, K, Ag and Sn in the glass surface layers, the specimens were etched in 2.5% HF solution. The loss in specimen thickness was measured with an accuracy of $\pm 0.5\mu\text{m}$ using a dial gauge.

The times of etching were chosen so as to remove layers ranging from 1 to $10\mu\text{m}$. The solution obtained from etching was evaporated dry under an IR lamp. The dry residue was dissolved in 2. ml. of concentrated HF and 1.5 ml. concentrated HClO_4 and re-evaporated dry under the IR lamp. The residue was dissolved in 5 ml of distilled water and introduced into a polythene sample bottle.

The samples prepared in this way were analyzed by atomic absorption spectrometry on the AA4 instrument by Varian-Techtron. The standard solutions were prepared from spectrally pure metals.

The concentration profiles of Na, K, Ag and Sn, Cu were also determined by the electron microprobe. A sample about $1 \times 10^{-4}\text{m}^2$ in area was cut out of the glass and its thickness measured. Pairs of the samples were glued together with the surfaces to be measured facing each other (in the case of Float glass, the „tinned” surfaces were thus joined), using the Lepox epoxy adhesive. Following thorough drying, the samples were ground on a diamond wheel under an angle of approx.

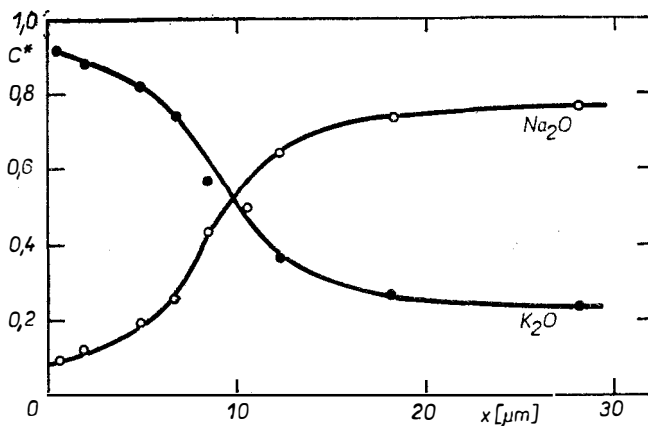


Fig. 2. The distribution of Na_2O and K_2O concentration following interaction of Float glass with KNO_3 melt (420°C , 24 h). The surface layer of glass formed in contact with the tin bath (atomic absorption).

45 degrees. The ground samples were further polished with cerium dioxide, provided with a vacuum-deposited carbon layer and analyzed by the JXA-5 electron microprobe.

MEASURING RESULTS

The experimental data are plotted in Fig. 2, which shows distribution the of Na₂O and K₂O following interaction of the Float glass with the KNO₃ melt. The melt was in contact with the „tinned” surface (that containing elevated amount of Sn) at 420 °C for 24 hours. The following figure shows the concentration profile of Na₂O and K₂O in the specimen which was in contact with the KNO₃ melt by the opposite surface under otherwise identical conditions. The concentrations of Na₂O and K₂O are given in relative values and their course is not identical on the two

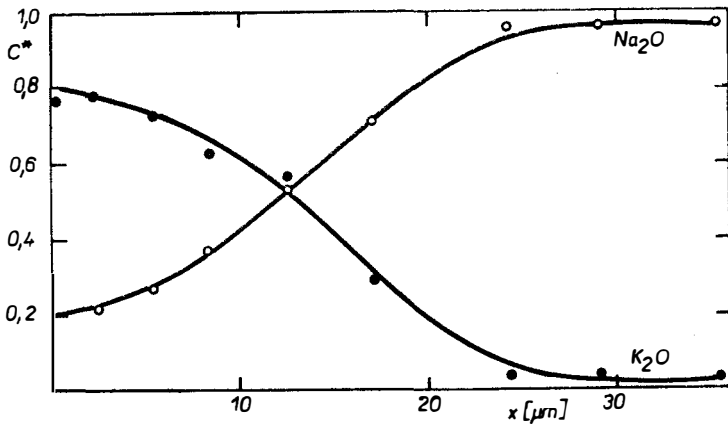


Fig. 3. The distribution of Na₂O and K₂O concentration following interaction the Float glass with KNO₃ (420 °C, 24 h). The surface layer of glass formed in contact with reduction atmosphere (atomic absorption).

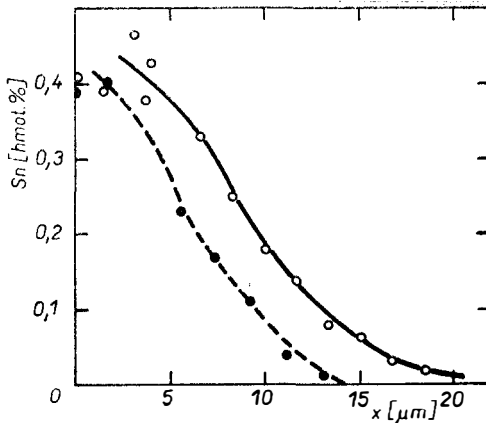


Fig. 4. The distribution of tin concentration in the original sample (○) and following interaction with KNO₃ (●) (elektron microprobe).

sides of the glass specimens. The fact that Sn takes part in the diffusion process is also borne out by Fig. 4 showing the concentration profile of Sn in the original Float glass (full line) and after interaction with the KNO_3 melt (dashed line). The interaction with KNO_3 melt at 420°C for 24 hours resulted in a distinct loss of tin in the surface layer.

Similar findings were obtained with the interaction of Float glass with the molten mixture of AgNO_3 and KNO_3 (20 mol% AgNO_3). The data are plotted in Figs 5—7.

In contrast to this, interaction of Float glass with the CuSO_4 -ochre mixture at 600°C for 30 minutes did not bring about any discernible change in tin concentration, even though the copper had penetrated into a depth of about $20\ \mu\text{m}$ (Fig. 8).

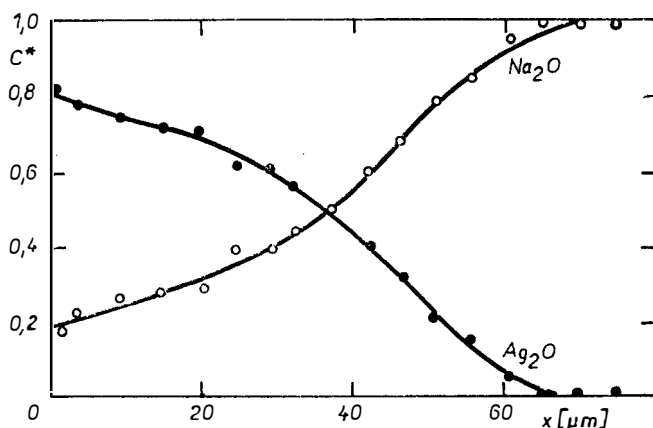


Fig. 5. The distribution of Na_2O and Ag_2O concentration following interaction with $\text{AgNO}_3 + \text{KNO}_3$ (350°C , 14 h) — surface layer of glass formed in contact with tin bath (electron microprobe).

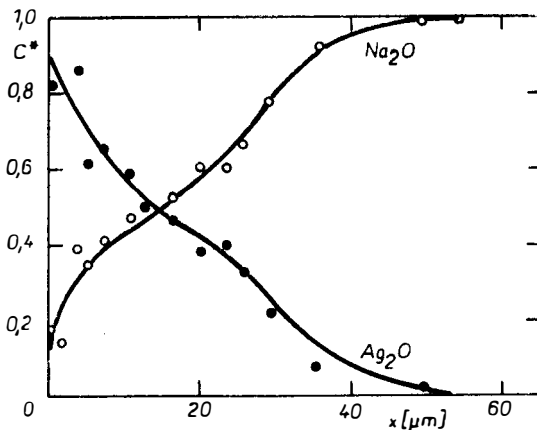


Fig. 6. The distribution of Na_2O and Ag_2O concentration following interaction of Float glass with $\text{AgNO}_3 + \text{KNO}_3$ melt (350°C , 14 h) — surface layer of glass formed in contact with reduction atmosphere (electron microprobe).

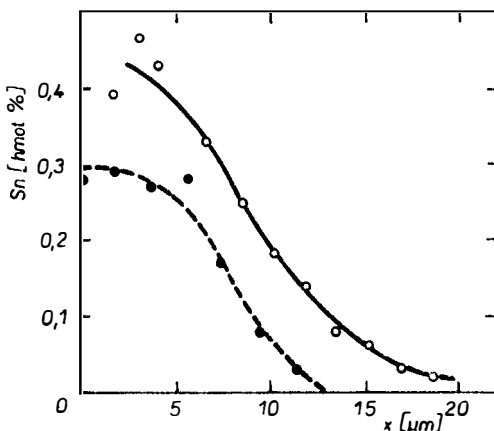


Fig. 7. The distribution of tin concentration in the original sample (○) and after its interaction with $\text{AgNO}_3 + \text{KNO}_3$ melt (●) (electron microprobe).

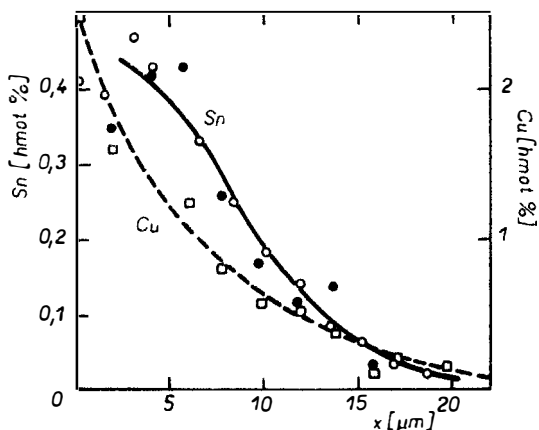


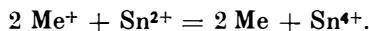
Fig. 8. The distribution of tin concentration in the original sample (○) and following interaction with the mixture of CuSO_4 with ochre (600°C , 30 minutes, full rings). The dashed line represents the distribution of copper after the interaction (□) (electron microprobe).

DISCUSSION

The natural explanation of the result is provided by the difference in the chemical composition of the by surface layers of Float glass. From the standpoint diffusion, sodium oxide is the main component. As follows from the literature, both surfaces of Float glass show a deficit of Na_2O . On first sight it might appear that the diffusion of foreign ions proceeds so that these must first overcome a certain distance over which the concentration of sodium ions is lower than in the deeper glass layers. However, the concentration profile does not in fact remain constant, being shifted towards the glass surface owing to the relative great ability

Na⁺ ions to move in the basic silicate skeleton. At the same time, the foreign ions enter in the surface layer of glass and proceed into the interior by diffusion. In view of the presumed electroneutrality of the glass surface layer, the substitution exchange mechanism is highly probable. The foreign ions thus substitute the sodium ones, which enter the other part of the diffusion system (e.g. the molten salt) at the boundary between the glass and the source of foreign ions. The movement of foreign ions and that of sodium ions are thus not independent and can be described mathematically by relationships known from the theory of binary diffusion. For such a macroscopic description one would have to know the value of the interdiffusion coefficient, which could be obtained either experimentally or by theoretical calculation using certain simplifying assumptions. In the case of a considerable difference in the mobility of the two ions taking part in the diffusion, local electric field has to be considered as an additional driving force beside diffusion [7].

Tin ions also participate in the diffusion on that side of Float glass whose surface layer contains tin, as shown by Figs. 4 and 7. The depletion of tin in the surface layer indicates that it is particularly the Me⁺ ⇌ Sn²⁺ type of exchange which will control the rate of diffusion on a very thin surface layer, whereas the significance of the Me⁺ ⇌ Na⁺ type of exchange will increase in the deeper layers of glass. If the foreign ion is liable to be reduced readily (e.g. Ag⁺ or Cu²⁺ and Cu⁺) the diffusion process can be made further more complex by an oxidation-reduction reaction; e.g. of the type



The problems of the reduction of silver ions in Float glass are dealt with in more detail by Shelby and Vitko [4].

A mathematical description based on diffusion taking place simultaneously by two exchange mechanisms and further complicated by reduction and nucleation of one of the diffusion particles has not yet been derived. A certain simplification is possible on the assumption that only the Me⁺ ⇌ Sn²⁺ type of exchange takes place in a very thin surface layer. Such a procedure would require more detailed data on the distribution of cations in a very thin surface layer of glass, which would have to be obtained by other methods, such as ESCA or SIMS.

CONCLUSION

The presence of tin in the surface layer of Float glass is the cause of a different behaviour of this type of glass during interaction with melts of KNO₃, AgNO₃ and a mixture of CuSO₄ and ochre. In contrast to other types of glass, also tin takes part in the interaction with the given substances at elevated temperature. The effect of tin is probably based on its participation in the exchange mechanism of diffusion of potassium and silver ions into the surface layer of the glass. In the case of silver and copper ions, reduction and nucleation caused by tin ions can likewise be involved.

References

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DIFÚZE V POVRCHOVÉ VRSTVĚ SKLA FLOAT

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Sklo Float se vyznačuje oproti ostatním komerčně vyráběným typům skla odlišným chemickým; složením povrchové vrstvy, zejména relativně vysokým obsahem cínu v povrchové vrstvě která je při jeho výrobě v kontaktu s roztaveným cínem. Cín se může ve skle vyskytovat v několika oxidačních stupních a může participovat na interakci povrchu skla s okolním prostředím.

Předpoklad participace cínu na interakci povrchu skla Float s taveninami roztavených solí, resp. se směsí CuSO_4 a okru byl ověřován tepelnou expozicí vzorků tohoto skla na zařízení, jehož schéma je na obr. 1. Po tepelné expozici vzorků byla v jejich povrchové vrstvě stanovena distribuce vybraných iontů. K tomu účelu bylo použito jednak metody postupného leptání a analýzy pomocí atomové absorpční spektroskopie a jednak elektronové mikrosondy. Výsledky těchto měření jsou shrnuty na obr. 2-8.

Experimentální údaje ukazují, že předpoklad participace cínu při interakci povrchu skla Float s taveninami KNO_3 a AgNO_3 je oprávněný. Účinek cínu pravděpodobně spočívá v tom, že se spolupodílí na výměnném mechanismu difúze draselných a stříbrných iontů do povrchové vrstvy skla. V případě iontů stříbra a mědi se může uplatňovat i redukce a nukleace ionty cínu.

Obr. 1. Schéma aparatury pro tepelnou expozici. 1 — trubková pec, 2 — stojan od Brabcovy pece, 3 — korundová trubka, 4 — tvarovka z alparitové cihly, 5 — kelímek z nerez oceli, 6 — držáček na vzorky, 7 — termočlánek Pt—PtRh, 8 — regulační termočlánek Fe—Co.

Obr. 2. Distribuce koncentrace Na_2O a K_2O po interakci skla Float s taveninou KNO_3 (420°C , 24 h) — povrchová vrstva skla vzniklá kontaktem s cínovou lázní (atomová absorpce).

Obr. 3. Distribuce koncentrace Na_2O a K_2O po interakci skla Float s taveninou KNO_3 (420°C , 24 h) — povrchová vrstva skla vzniklá kontaktem s redukční atmosférou (atomová absorpce).

Obr. 4. Distribuce koncentrace cínu v původním vzorku (●) a po interakci s taveninou KNO_3 (○) (elektronová mikrosonda).

Obr. 5. Distribuce koncentrace Na_2O a Ag_2O po interakci skla Float s taveninou $\text{AgNO}_3 + \text{KNO}_3$ (350°C , 14 h) — povrchová vrstva skla vzniklá kontaktem s cínovou lázní (elektronová mikrosonda).

Obr. 6. Distribuce koncentrace Na_2O a Ag_2O po interakci skla Float s taveninou $\text{AgNO}_3 + \text{KNO}_3$ (350°C , 14 h) — povrchová vrstva skla vzniklá kontaktem s redukční atmosférou (elektronová mikrosonda).

Obr. 7. Distribuce koncentrace cínu v původním vzorku (○) a po jeho interakci s taveninou $\text{AgNO}_3 + \text{KNO}_3$ (●) (elektronová mikrosonda).

Obr. 8. Distribuce koncentrace cínu v původním vzorku (○) a po interakci se směsí CuSO_4 + okru (600°C , 30 minut-plné kroužky). Čárkovaná křivka znázorňuje distribuci mědi po interakci (□). (elektronová mikrosonda).

ДИФФУЗИЯ В ПОВЕРХНОСТНОМ СЛОЕ СТЕКЛА FLOAT

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Стекло Float выделяется по сравнению с другими типами стекла, находящимися в продаже, отличительным химическим составом поверхностного слоя, именно относительно высоким содержанием свинца в поверхностном слое, который при его производстве находится в соприкосновении с расплавленным свинцом. Свинец в стекле может появляться в нескольких степенях окисления и может принимать участие во взаимодействии поверхности стекла с окружающей средой.

Предположение участия свинца во взаимодействии поверхности стекла Float с расплавами расплавленных солей, или со смесью Cu_2O - и охры проверяли термической выдержкой проб данного стекла на установке, схема которой приводится на ри. 1.

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После термической выдержки проб в их поверхностном слое устанавливали распределение выбранных ионов. Для заданной цели использовали с одной стороны метод постепенного травления и анализа с помощью атомной абсорбционной спектроскопии, а с другой стороны электронные микронзонды. Результаты приводимых измерений сопоставляются на рис. 2--8.

Экспериментальные данные показывают, что предположение участия свинца во взаимодействии поверхности стекла Float с расплавами KNO_3 и AgNO_3 вполне оправдано. Действие свинца со всей правдоподобностью заключается в том, что он принимает участие в обменном механизме диффузии калиевых и серебряных ионов в поверхностный слой стекла. В случае ионов серебра и меди может действовать даже восстановление и нуклеация, вызываемая ионами свинца.

Рис. 1. Схема аппаратуры, предназначенной для термической выдержки.

Рис. 2. Распределение концентрации Na_2O и K_2O по взаимодействию стекла Float с расплавом KNO_3 (420°C , 24 ч.) -- поверхностный слой, образовавшийся в результате взаимодействия с свинцовой ванной (атомная абсорбция).

Рис. 3. Распределение концентрации Na_2O и K_2O после взаимодействия стекла Float с расплавом KNO_3 (420°C , 24 ч.) -- поверхностный слой стекла, образовавшийся в результате взаимодействия с восстановительной средой (атомная абсорбция).

Рис. 4. Распределение концентрации свинца в исходной пробе (o) и после взаимодействия с расплавом KNO_3 (●) — (электронный микронзонд).

Рис. 5. Распределение концентрации Na_2O и Ag_2O после взаимодействия стекла Float с расплавом $\text{AgNO}_3 + \text{KNO}_3$ (350°C , 14 ч.) — поверхностный слой, образовавшийся в результате взаимодействия со свинцовой ванной (электронный микронзонд).

Рис. 6. Распределение концентрации Na_2O и Ag_2O после взаимодействия стекла Float с расплавом $\text{AgNO}_3 + \text{KNO}_3$ (350°C , 14 ч.) — поверхностный слой стекла, образовавшийся в результате взаимодействия с восстановительной средой (электронный микронзонд).

Рис. 7. Распределение концентрации свинца в исходной пробе (o) и после его взаимодействия с расплавом $\text{AgNO}_3 + \text{KNO}_3$ (●) (электронный микронзонд).

Рис. 8. Распределение концентрации свинца в исходной пробе (o) и после взаимодействия со смесью CuS ●- = охра (600°C , 30 минут — полные кружочки). Штриховая кривая изображает распределение меди после взаимодействия (—). (электронный микронзонд).