

Diffusion colouring of glass with silver ions

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Surface colouring of glass through an exchange of sodium for silver ions has been studied. The influence of the main parameters of thermal treatment on the spectral properties of glass has been observed. The following techniques were applied: UV-VIS spectroscopy, differential thermal analysis (DTA), scanning electron microscopy (SEM) with energy disperse X-ray analysis (EDX) and photoelectron spectroscopy (XPS). Surface distribution as well as the chemical state of silver ions at different stages of thermal treatment has been investigated. The influence of the reduction atmosphere and ionizing radiation on glass colour and the chemical state of silver has also been studied. New information on glass colouring due to silver diffusion in one of the oldest colouring techniques has been obtained. It has been found that silver is present mainly in the form of AgO and Ag₂O. In reduction conditions silver forms metallic particles with the mean size of 0.7 μm. Great chemical changes in the near surface region have been observed.

Keywords: diffusion, glass, silver, XPS.

1. Introduction

The process of staining enables selective interaction only on selected areas of the glass surface and its colouring. This is a substantial advantage of the method, which makes it particularly important in the production technology of coloured glass. The modern research techniques allow us to obtain new, detailed information about this process [1]–[3] and conditions of its application in the present-day production technology [4].

The object of the investigations was the process of glass colouring with silver compounds by way of surface exchange of ions (staining).

2. Experimental procedure

The base material in the performed investigations was glass of the composition (wt%): SiO₂ (70.8), Al₂O₃ (1.9), CaO (8.2), MgO (4.4), Na₂O (13.9), K₂O (0.4), SO₃ (0.3). On the basis of DTA investigations the characteristic temperatures of the glass were

determined: $T_t = 558\text{ }^\circ\text{C}$, $T_s = 598\text{ }^\circ\text{C}$. Glass plates measuring $76 \times 26 \times 2\text{ mm}$ were used in the tests. The composition of the paste prepared for staining was as follows: $\text{MnO}_2 : \text{Fe}_2\text{O}_3 : \text{Ag}_2\text{SO}_4 = 2.5 : 2.5 : 1$ (mass fractions). The paste in the form of a suspension in turpentine oil and turpentine was deposited on the base plates by the method of spraying. The program for drying and firing was prepared on the basis of DTA of the base glass and the staining paste. The investigations were carried out at the temperature range of $460\text{--}700\text{ }^\circ\text{C}$ and the firing time $10\text{--}60\text{ min}$. A constant rate of temperature increase $10\text{ }^\circ\text{C}/\text{min}$ and isothermic treatment at the set parameters were applied. DTA investigations were conducted on Q-1500D derivatograph, using the standard rate of temperature increase $10\text{ }^\circ\text{C}/\text{min}$. The transmission of the samples in the range of ultraviolet and visible light was determined on UV-VIS Hewlett Pacard 8453 spectrophotometer. Microscopic observations were conducted on Joel 5400 electron microscopy equipped with Link ISIS 300 X-ray microanalyser. Photoelectron spectroscopy investigations were carried out on VSW spectrometer with a hemispherical analyser operating in FAT 22 mode. The source of X-ray radiation was a lamp with an aluminium cathode – Al, K_α of the power 200 W (10 kW , 20 mA). The analysis of XPS spectra was realized using XPSPEAK programme, version 4.1. The spectra were calibrated basing on the position of the carbon $\text{C}1s = 284.6\text{ eV}$. Depth profiling was realized using argon ion gun operating at the following parameters: accelerating voltage – 2 keV , current – 1 mA .

3. Results and discussion

The result of thermal treatment was the surface colouring of glasses of various intensities, from bright yellow to intensive amber-like colour, depending on temperature and time of treatment. Investigations by means of X-ray microanalyser have shown that the homogeneity of the diffusion layer increases with the increase in temperature and time of thermal treatment. In samples heated at lower temperatures silver forms agglomerations of $5\text{--}20\text{ }\mu\text{m}$. An increase in the temperature of isothermal treatment or in the heating time results in a more uniform distribution of silver ions in

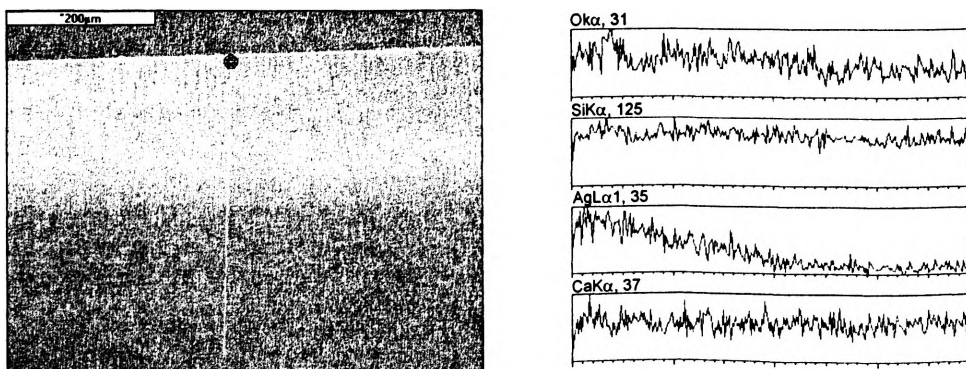


Fig. 1. Distribution of silver on the transverse fracture of a sample after the treatment at $600\text{ }^\circ\text{C}$ for 30 min .

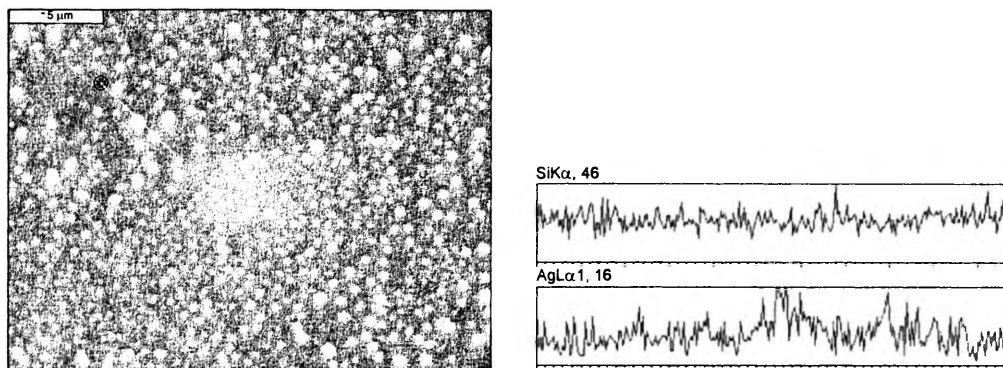


Fig. 2. Distribution of silver on the sample surface after the treatment at 500 °C for 30 min under reducing conditions.

the glass structure. The observed inhomogeneities of silver distribution on the glass surface may be due to structural differences in glass leading to energetic differentiation of its surface. This hypothesis, however, can only be confirmed after further investigations carried out on glasses of different chemical compositions. The depth of silver penetration inside the glass determined from microscopic investigations amounts to 150 μm for a sample fired at the temperature of 600 °C during 30 min (Fig. 1). A great influence of the conditions (reduction, oxidizing) of thermal treatment on the colour and morphology of the obtained layers was noticed. Microscopic observations of the surface have revealed the formation, under reduction conditions, of metallic silver agglomerations, 0.5–1 μm in size, distributed uniformly on the surface (Fig. 2). Such agglomerations have not been observed in the samples treated under oxidizing conditions. Figure 3 shows the transmittance of samples obtained after

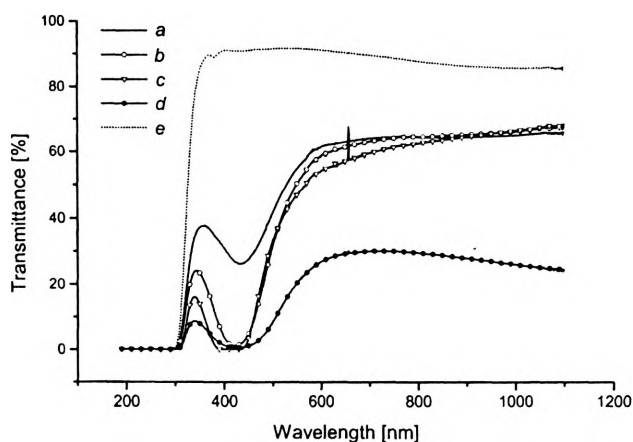


Fig. 3. Transmittance curves of samples: after the treatment at 550 °C for 30 min (a), after the treatment at 600 °C for 30 min (b), after the treatment at 700 °C for 30 min (c), after the treatment at 550 °C for 30 min, under reduction conditions (d), base glass (e).

treatment at the temperatures of: 550, 600, 700 °C during 30 min in oxidizing conditions, and the transmittance of a sample obtained in reduction conditions (550 °C, 30 min). The transmittance becomes reduced with the temperature of the sample. The main absorption band occurs in the range of 350–500 nm, with maximum at 430 nm, which corresponds to the amber-like colour. The transmittance of the sample obtained under reduction conditions is characterized by a broader absorption band (350–600 nm) and high absorption in the infrared range – above 650 nm (Fig. 3).

Colouring obtained by way of staining from a silver paste shows high sensitivity to X-ray radiation, which has been observed on samples after XPS investigations. X-ray radiation causes a change in the sample transmittance, resulting from the reduction of silver at the irradiated places. Reduction of silver ions to metallic silver in sodium-calcium glass has also been confirmed by the investigations of YOSHIMURA, *et al.* [3].

Photoelectron spectroscopy investigations combined with the ion sputtering technique enabled us to establish the chemical composition of the diffusion layer and to determine the depth of silver diffusion to glass. XPS spectra for the region of silver

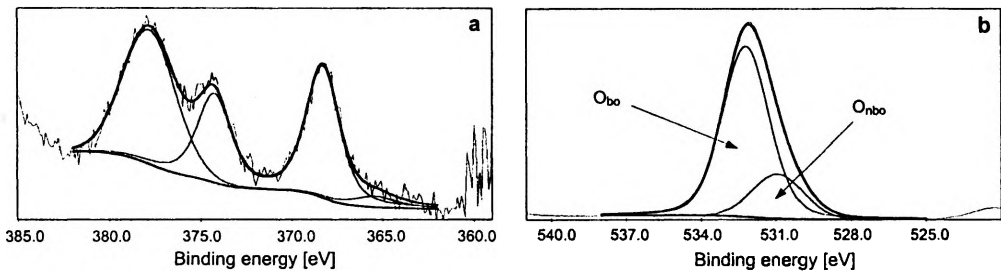


Fig. 4. XPS spectra of the sample at 550 °C/30 min: region of silver and potassium (a), region of oxygen O1s (b), where O_{bo} – bridging oxygen, O_{nbo} – non-bridging oxygen.

High potassium concentration layer $Na^+ + K^+ + Ag^+$
Low alkalis concentration layer $Si^{4+} + Ag^+$
$Na^+ + Si^{4+} + Ag^+$
Glass bulk

Fig. 5. Model of the silver diffusion layer.

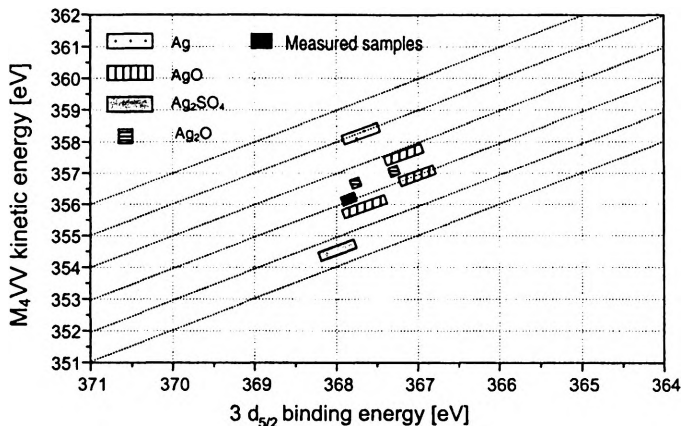


Fig. 6. Determination of the degree of silver oxidation from Auger parameter.

and potassium are shown in Fig. 4a, and those for the region of oxygen – in Fig. 4b. The depth of silver diffusion determined from the measurements of silver concentration as a function of depth was equal to about 150 μm for a sample obtained in optimal conditions (the greatest density of colour at 600 $^{\circ}\text{C}$, 30 min). Basing on the chemical distribution of elements at the analysed depth, a model of the diffusion layer, shown in Fig. 5, was developed. In the upper layer there dominate the alkaline ions, mainly sodium and potassium. The highest concentration of silver ions is observed here. Next, the concentration of the alkaline ions decreases below the value characteristic of glass composition. Silicon dominates here, and the concentration of silver ions is lower, although still high. When steadily lowering, the concentration of silver finally reaches zero, whereas the concentration of alkaline ions and silicon corresponds to the content of these elements in glass. A high agreement between the amount of the non-bridging oxygens and the chemical composition of glass, mainly the content of alkalis, can be observed. In the upper layer with a great number of defects of the broken bonds type and increased concentration of alkalis, the number of non-bridging oxygens is the highest. The smallest amount of the non-bridging oxygens is found in the “second” layer, characterized by a small content of alkalis and a great amount of silicon, which results in a highly polymerized structure with a great number of the bridging oxygens.

When applying the XPS, the authors attempted to determine the degree of oxidation of the silver ions in glass. In the professional literature the opinions referring to this problem vary greatly. An opinion can be found that the observed colour of glass derives from metallic silver of colloidal dispersion. To solve this problem the so-called Auger parameter was used [5], [6]. The obtained results have not confirmed the presence of metallic silver in glasses heated in oxidizing atmosphere. The most probable is the occurrence of silver at the second and first degree of oxidation (Fig. 6). The authors believe that these amounts are comparable. Unambiguous solution, however, is not possible [6].

4. Conclusions

The following conclusions can be drawn from our investigations:

1. Staining represents an effective method of colouring and it enables us to obtain a wide spectrum of yellow glasses through the selection of the composition of a staining paste and conditions of thermal treatment.

2. In the investigation conditions the diffusion of silver to the depth of about 150 μm has been obtained. The diffusion layer has a composite character; the near surface region is enriched with potassium and it contains maximal amount of silver, below it there is a zone of a smaller content of alkaline ions, which gradually passes into the region of not transformed base glass.

3. Silver occurs at the oxidation degree +2 and +1. In samples obtained under oxidizing conditions the presence of metallic silver is not observed.

4. Thermal treatment carried out under reduction conditions leads to the reduction of Ag^{2+} silver to Ag^+ . In the near surface layers silver occurs in the metallic form Ag^0 as a colloid with particles diameters 0.5–1 μm .

5. Photoelectron spectroscopy investigations combined with ionic etching have revealed varying content of the non-bridging oxygens, correlated with changes in the chemical composition in the diffusion layer.

References

- [1] ROY B., JAIN H., ROY S., CHAKRAVORTY D., *J. Non-Cryst. Solids* **222** (1997), 102.
- [2] WANG P.W., *Appl. Surf. Sci.* **120** (1997), 291.
- [3] YOSHIMURA E.M., OKUNO E., KRAJCZYK L., SUSZYNSKA M., *Nucl. Instrum. Methods Phys. Res. B* **141** (1998), 304.
- [4] TAKEDA S., YAMAMOTO K., MATSUMOTO K., *J. Non-Cryst. Solids* **265** (2000), 133.
- [5] SCHON G., *Electron. J. Spectrosc.* **2** (1973), 75.
- [6] WAGNER C.D. [Ed.], *Handbook of X-ray Photoelectron Spectroscopy*, Perkin–Elmer Corp., 1979.

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