

Původní práce

DIFFUSION OF SILVER INTO  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  GLASS FROM  $\text{AgNO}_3$   
MELT

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*The changes in chemical composition of the surface layer of the base glass resulting from diffusion of silver from  $\text{AgNO}_3$  melt at  $350^\circ\text{C}$  are characterized by the content of Ag and its concentration profile in the glass. On the basis of these data the values of diffusion coefficients of silver and their dependence on the concentration of silver in glass were calculated.*

INTRODUCTION

The diffusion of silver into the surface layers of glass was established empirically already in the last century and studied in detail in the work by Schulze [1]. This study has initiated the experimental approach to the problems of diffusion of silver in glass and pointed out the fundamental problems which can be briefly summarized as follows:

- a) determination of concentration changes in the glass surface layer and their mathematical interpretation;
- b) formulation of the concept of the mechanism of diffusion of silver in glass;
- c) the possibility of accelerating and controlling the diffusion process;
- d) experimental determination and mathematical interpretation of the changes in the properties of basic glass taking place as a result of the diffusion of silver.

The above problems have not yet been solved satisfactorily, although many new data representing a substantially deeper understanding have been accumulated since the pioneer work by Schulze. The more recent data on the diffusion of silver in glass have been summarized in several comprehensive studies. Mention can be made for instance of the monography by Yevstrop'yev [2], Frischat [3] or the comprehensive report by Terai and Hayami [4].

The present study deals with the changes in chemical composition of the surface layer of  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  glass during the diffusion of silver. These changes are characterized by the content of silver and its concentration distribution and their experimental determination together with the mathematical interpretation is aimed at verifying the suitability of these parameters for the inspection and control of the technological processes serving for the preparation of defined diffusion layers on glass.

## EXPERIMENTAL

### Apparatus and working procedure

The diffusion cell in which glass specimens were thermally exposed is shown in the diagram in Fig. 1. The glass specimen fitted to glass rod 5 was submerged by about 2/3 in  $\text{AgNO}_3$  melt placed in test-tube 2 situated at the bottom of an external quartz glass tubular sheath 4 lined with asbestos. During thermal exposure of the specimen the apparatus was placed in a vertical electric resistance furnace, the temperature of which was kept at  $350 \pm 5^\circ\text{C}$  by means of a chopper-bar controller. The temperature was measured by a Pt—Pt 10 Rh thermocouple the hot end of which was placed in a protective quartz glass tube closely at the melt level.

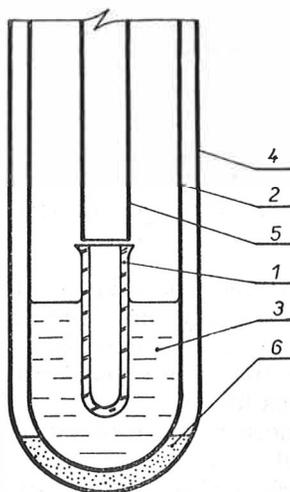
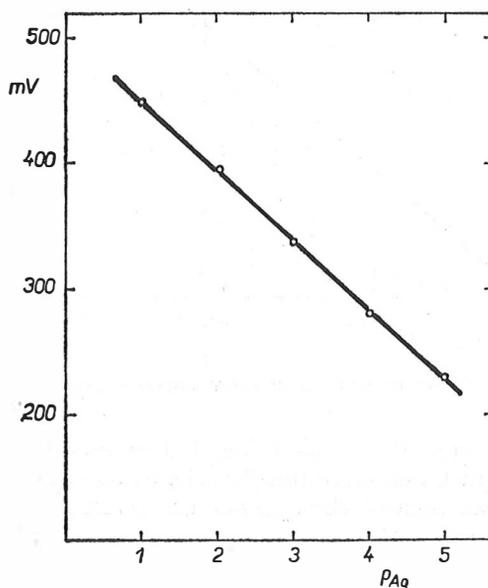


Fig. 1. The diffusion cell; 1 — glass sample, 2 — internal test-tube, 3 —  $\text{AgNO}_3$  melt, 4 — external quartz tube, 5 — glass tube for specimen fixing, 6 — asbestos lining.

The experimental work was carried out with binary glass having the molar composition of  $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$  which was prepared in laboratory by fusion of sodium carbonate A.R. and T 13 glass sand in a platinum crucible. The molten glass was shaped into specimens having the form of small test-tubes of 15 mm OD, wall thickness of approx. 1.5 mm and about 18 mm in length, which were then placed in a desiccator over silicagel.

Before the exposure proper the glass specimen was rinsed in ethyl alcohol, dried and fixed with silver wire to the supporting tube. The internal test-tube was filled with finely ground silver nitrate and placed in the furnace. After attaining the working temperature the specimen was immersed in the melt, removed after the required period of time, cooled in air, washed with distilled water and rinsed with ethyl alcohol. The top and bottom sections of the specimens chosen for the determination of total amount of silver were cut off

with diamond discs. The extreme ends of the specimens which may have been subjected to interfering effects during exposure were thus removed and the specimen was simultaneously adjusted to a cylindrical shape of defined surface area. These specimens were etched in a 2 % HF solution stirred with a magnetic agitator and the extract was evaporated dry. The evaporation residue was dissolved in 2–4 ml mixture of concentrated HF and HClO<sub>4</sub> (2 : 1.5), reevaporated dry and dissolved in 10 ml distilled water. The completeness of etching off the silver containing layer was checked by reetching and determining silver in the resulting solution. The solutions were kept in polyethylene vessels and analyzed in series by means of an ionic selective silver electrode. This electrode was used in system with saturated calomel electrode and a salt bridge of saturated KNO<sub>3</sub> solution. The measurements were evaluated by means of a standard diagram prepared with the use of standard AgNO<sub>3</sub>



*Fig. 2.* Standard diagram of the silver ion-selective electrode.

solutions in concentrations ranging from 10<sup>-1</sup>–10<sup>-6</sup> M. An example of such a standard diagram is shown in Fig. 2.

For the purpose of determining the concentration profile of silver in the glass a section of the exposed sample was cast in an epoxy resin, ground with firmly bound abrasive (22, 10, 5 μm) and polished with cerium oxide. Then an electrically conductive carbon layer was deposited in vacuo and the sample analyzed with an electron microprobe at steps of 20–40 μm. The concentration of silver was determined by means of simultaneous measurements of AgSe-based standards of known silver content.

THE RESULTS AND DISCUSSION

The data on the content of silver in the glass surface layer are plotted in Fig. 3 in the form of dependence on the second root of time. The experimental points are means of 4—5 determined values the dispersion of which had not exceeded 10 %. The linear relationship in Fig. 3 indicates that the process

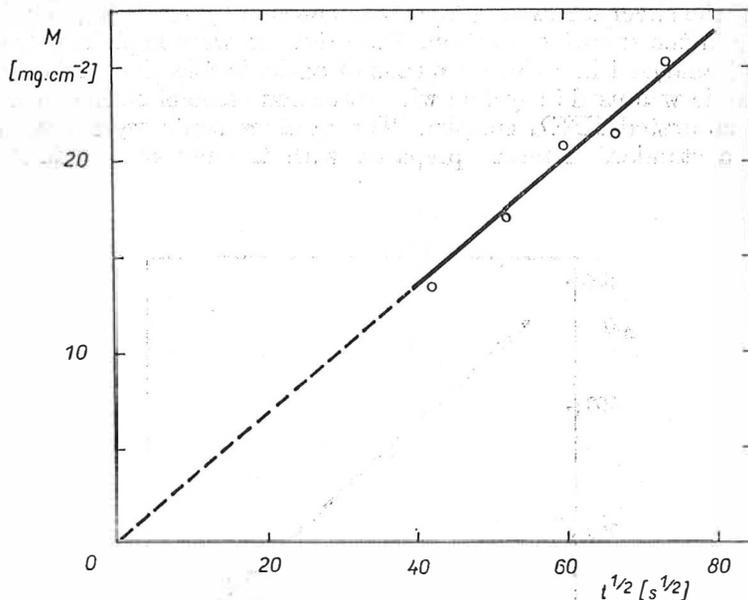


Fig. 3. Silver content in glass vs. second root of time.

is controlled by diffusion. When assuming that at the glass surface a constant concentration of silver  $C_0$  is maintained in the course of diffusion, the content of Ag per unit surface area of the specimen is given by the relation

$$M = 2C_0 \sqrt{\frac{Dt}{\pi}}, \tag{1}$$

where  $D$  is the diffusion coefficient and  $t$  is the time of diffusion. The diffusion coefficient  $D$  can be calculated when the surface concentration  $C_0$  is known. The surface concentration was determined by means of the experimentally established concentration profile of silver in the glass surface layer which may be described mathematically by the following equation:

$$C = C_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{2}$$

where  $x$  is the diffusion distance. By introducing the parameter  $\frac{x}{2\sqrt{t}}$  identical curves of concentration distribution for any arbitrary time of diffusion are

obtained. Fig. 4 shows the dependence of  $C$  on the given parameter for the periods of time of 30 and 60 minutes obtained by electron probe measurements. Although a certain disagreement of concentration profiles for the given period of time may be observed in regions more distant from the surface, the approximate surface concentration value  $C_0 = 1.0 \text{ g cm}^{-3}$  can be extrapolated with a satisfactory accuracy. Using this value equation (1) yields  $D = 7.8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  which should be considered an orientation value only. When this diffusion coefficient has been substituted into equation (2) the calculated concentration values do not agree with the data established experimentally.

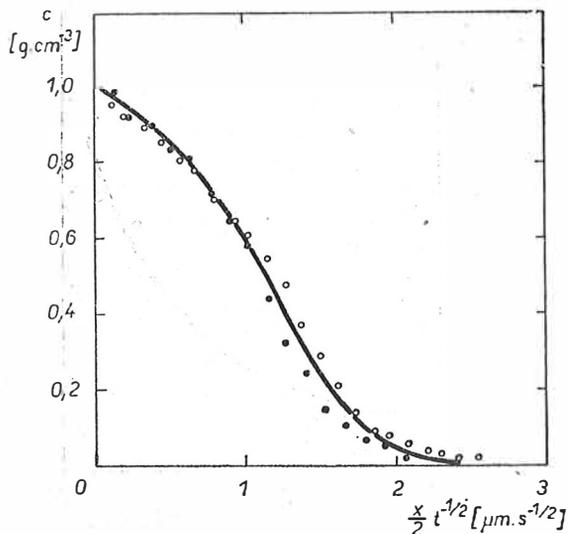


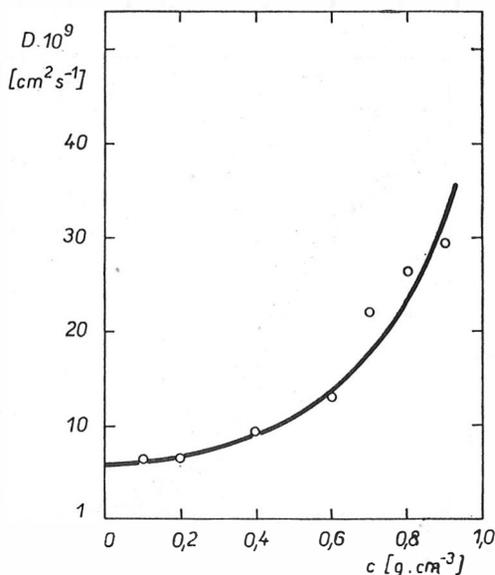
Fig. 4. Silver concentration distribution in glass for period of 60 (●) and 90 (○) minutes.

The concentration of silver in the glass surface layer attains relatively high values which allows to assume that this disagreement is due to a dependence of the diffusion coefficient on concentration. The simple form of the II<sup>nd</sup> Fick's law which does not take into account the dependence of the diffusion coefficient on concentration thus obviously does not hold and neither does equation (2) which has been derived from it. An exact solution of the diffusion process in question would therefore require to consider the change in glass density in terms of silver concentration. These data are not available so that we have chosen the procedure according to the Boltzmann—Matan method [5] which considers the dependence of the diffusion coefficient on concentration when neglecting the changes in glass density. The diffusion coefficient is then given by the equation

$$D = -2 \left( \frac{d\eta}{dC} \right)_c \int_0^C \eta dC, \tag{3}$$

where  $\eta = \frac{x}{2 \sqrt{t}}$ .

The data required for the calculation of the diffusion coefficient according to equation (3) were determined graphically from the relationship in Fig. 4. The calculated  $D$  values in terms of concentration of silver in glass are plotted in Fig. 5. The diffusion coefficient increases with increasing silver concentration in particular in the region of higher concentration values. The  $D$  value determined from the content of silver in glass is somewhat higher as compared with the values in Fig. 5 and corresponds to the higher-than-expected concentration value.



*Fig. 5.* The diffusion coefficient of silver vs. concentration.

The diffusion coefficients of silver in binary glasses of the system  $Na_2O \cdot 2SiO_2$  were determined by Malinin, Yestropyev and Chechomsky [6] by means of the thin layer method so that their values may be compared with the value obtained from Fig. 5 by extrapolating the dependence of  $D$  to zero silver concentration in glass. The highest  $Na_2O$  content in the binary glasses employed by Malinin was 25 mole %. The results have therefore to be extrapolated for

*Table 1*

The values of diffusion coefficients

	$D$ [ $cm^2 s^{-1}$ ]	Glass composition [mole %]	Note
Malinin[6]	$D_{Ag} = 8 \times 10^{-10}$	25 $Na_2O$ , 75 $SiO_2$	—
Malinin[6]	$D_{Ag} = 3 \times 10^{-9}$	34 $Na_2O$ , 66 $SiO_2$	extrapolated
The present study	$D_{Ag} = 6 \times 10^{-9}$	34 $Na_2O$ , 66 $SiO_2$	extrapolated
Terai[4]	$D_{Na} = 1 \times 10^{-9}$	34 $Na_2O$ , 66 $SiO_2$	—

the value of 34 mole %  $\text{Na}_2\text{O}$  corresponding to the glass employed in the present study. The comparison is shown in Table I including also the data on the diffusion coefficient of sodium. In view of the fact that the comparable data have been obtained by extrapolation the agreement of the diffusion coefficients of silver may be considered satisfactory. It is also obvious that the diffusion coefficient of sodium in the given glass is higher than that of silver for a very low concentration of silver in glass but does not attain the values of  $D_{\text{Ag}}$  at higher silver concentration ( $D_{\text{Na}} = D_{\text{Ag}}$  at  $C_{\text{Ag}} = \text{approx. } 0.4 \text{ g cm}^{-3}$ ). It is therefore possible to assume that in the relationship for „interdiffusion coefficient“ [7]

$$\tilde{D} = \frac{D_{\text{Ag}}D_{\text{Na}}}{N_{\text{Ag}}D_{\text{Ag}} + N_{\text{Na}}D_{\text{Na}}} \left[ 1 + \frac{\partial \ln \gamma_{\text{Ag}}}{\partial \ln N_{\text{Ag}}} \right], \quad (4)$$

where  $N_i$  is the molar fraction of the respective component, the dependence of the activity coefficient of silver ions  $\gamma_{\text{Ag}}$  should be considered in terms of concentration.

In view of the low solubility of silver in silicate glasses the maximum silver concentration attained in the glass is relatively high ( $1.0 \text{ g cm}^{-3}$ ). It may be assumed that in agreement with the conclusions by Schulze [1] which have been verified by other authors the value is attained because of the simultaneous diffusion of sodium ions from glass into the  $\text{AgNO}_3$  melt. The surface silver concentration value found in this work indicates that in the given glass only about more than one third of sodium ions (approx. 36 %) have been replaced by silver ions. It therefore appears that in a simple binary glass all the sodium ions are not equivalent from the point of view of bond intensity in the structural glass lattice or from the point of view of their spatial accessibility to silver ions.

### CONCLUSION

The content of silver and its concentration profile in the  $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$  glass was determined after silver has been allowed to diffuse from silver nitrate melt at  $350^\circ \text{C}$  and the diffusion coefficient of silver in glass were determined from the data obtained. The diffusion coefficient of silver depends on its concentration in glass and within the concentration range of  $0\text{--}1.0 \text{ g cm}^{-3}$  it attains the values of  $6.0 \times 10^{-9}\text{--}5.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . The minimum diffusion coefficient value is in a satisfactory agreement with published data. Preparation of layers with a defined content and distribution of silver should be based on the dependence of the diffusion coefficient of silver on concentration at the given temperature.

### Acknowledgement

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## DIFÚZE STŘÍBRA DO SKLA $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ Z TAVENINY $\text{AgNO}_3$

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Za teploty 350 °C byl zkoumán proces difúze stříbra z taveniny  $\text{AgNO}_3$  do skla o molárním složení  $\text{NaO} \cdot 2\text{SiO}_2$ . Změna složení povrchové vrstvy byla určena stanovením obsahu a rozdělení koncentrace stříbra ve skle. Obsah stříbra ve skle byl určen odleptáním povrchové vrstvy a stanovením koncentrace stříbra ve vzniklém roztoku pomocí selektivní stříbrné elektrody. Rozdělení koncentrace stříbra ve skle bylo určeno na elektronové mikrosondě.

Obsah stříbra v povrchové vrstvě skla je lineární funkcí druhé odmocniny z času. Pomocí vztahu (1) byla určena hodnota difúzního koeficientu stříbra  $D = 7,8 \cdot 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ . Extrapolací koncentračního profilu k povrchu skla byla určena hodnota povrchové koncentrace stříbra  $C_0 = 1,0 \text{ g} \cdot \text{cm}^{-3}$ . Použitím Boltzmanovy—Matanovy metody byla stanovena z koncentračního profilu závislost difúzního koeficientu stříbra na koncentraci. Pro oblast koncentrace 0— $1,0 \text{ g} \cdot \text{cm}^{-3}$  nabývá difúzivita hodnot  $6,0 \cdot 10^{-9} — 5,5 \cdot 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ . Porovnání difúzních koeficientů nalezených různými autory je v tabulce I. Výsledky práce ukazují, že při přípravě povrchových vrstev s definovaným obsahem a rozdělením stříbra je třeba vycházet ze závislosti difúzního koeficientu stříbra na koncentraci za dané teploty.

*Obr. 1.* Difúzní cela; 1 — vzorek skla, 2 — vnitřní zkumavka, 3 — tavenina  $\text{AgNO}_3$ , 4 — vnější trubice z křemenného skla, 5 — skleněná trubice pro upevnění vzorku, 6 — azbestové lůžko.

*Obr. 2.* Kalibrační graf stříbrné iontové selektivní elektrody.

*Obr. 3.* Závislost obsahu stříbra ve skle na druhé odmocnině z času.

*Obr. 4.* Rozdělení koncentrace stříbra ve skle pro časy 60 (●) a 90 (○) minut.

*Obr. 5.* Závislost difúzního koeficientu stříbra na koncentraci.

## ДИФФУЗИЯ СЕРЕБРА В СТЕКЛЕ $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ ИЗ РАСПЛАВА $\text{AgNO}_3$

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Исследовали процесс диффузии серебра из расплава  $\text{AgNO}_3$  в стекло молярного состава  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  при температуре 350 °C. Изменение состава поверхностного слоя определяли установлением содержания и распределения концентрации серебра в стекле. Содержание серебра в стекле определяли травлением поверхностного слоя и определением концентрации серебра в образовавшемся растворе с помощью ионно-избирательного серебрянного электрода. Распределение концентрации серебра в стекле определяли посредством микрозонда.

Содержание серебра в поверхностном слое стекла является линейной функцией второго корня из времени. На основании отношения (1) определяли величину коэффициента диффузии серебра  $D = 7,8—10^{-8} \text{ см}^2 \cdot \text{с}^{-1}$ . Экстраполяцией концентрационного профиля к поверхности стекла определяли величину поверхностной концентрации серебра  $C_0 = 1,0 \text{ г} \cdot \text{см}^{-3}$ . С помощью метода Больцмана-Матана установили на основании

концентрационного профиля зависимость коэффициента диффузии серебра от концентрации. Для области концентрации 0—1,0 г. см<sup>-3</sup> достигает диффузивность величин  $6,0 \cdot 10^{-9}$  —  $5,5 \cdot 10^{-8}$  см<sup>2</sup>. с<sup>-1</sup>. Сопоставление коэффициентов диффузии, установленных разными авторами, приводится в таблице I. Результаты предлагаемой работы показывают, что при приготовлении поверхностных слоев с установленным содержанием и распределением серебра оказывается необходимым исходить из зависимости коэффициента диффузии серебра от концентрации при данной температуре.

*Рис. 1. Камера диффузии: 1 — проба стекла, 2 — внутренний химический стакан, 3 — расплав AgNO<sub>3</sub>, 4 — внешняя трубка из кварцевого стекла, 5 — стеклянная трубка для укрепления пробы, 6 — асбестовая подушка.*

*Рис. 2. График калибровки серебряного ионно-селективного электрода.*

*Рис. 3. Зависимость содержания серебра в стекле от второго корня из времени.*

*Рис. 4. Распределение концентрации серебра в стекле для времен 60 (●) и 90 (○) минут.*

*Рис. 5. Зависимость коэффициента диффузии серебра от концентрации.*