Original Papers

DISTRIBUTION OF THE CONCENTRATION OF SILVER IN SURFACE LAYER OF SIMAX GLASS

JOSEF MATOUŠEK, MARTIN MARYŠKA

Department of Glass and Ceramics, Institute of Chemical Technology, Technická 5, 166 28 Prague 6

Received Received 16. 9. 1991

Silver ions were incorporated into the surface of Simax glass at 335° C under the effect of a constant direct current (10–40 mA). The distribution of silver ions was determined in the surface layers obtained. Concentration profiles prepared at higher direct current values ($I \geq 20$ mA) are distinguished for rectangular shape e.g. diffusion movement of silver ions can be neglected and the concentration distribution in the surface layers is practically homogenous. The thickness of such kind of surface layers can be predicted theoretically if the corresponding velocity of shift of concentration edge is known. Theoretical calculations are in satisfactory agreement with the values determined experimentally. Concentration profiles originated at lower direct current values ($I = 10$ and 15 mA resp.) can be considered as a sum of diffusion movement and a shift of silver ions due to the influence of electrical field.

INTRODUCTION

The chemical composition of surface layers of glass can be modified by incorporation of foreign ions. The usual method is to do this by ionic diffusion, effected by interaction between the glass surface and a source of the respective ions. The distribution of the foreign ions in the glass surface is of a diffuse character. With Simax-type glasses, the diffusion coefficients of the foreign ions show relatively low values [1–3]. The diffusion layers are therefore thin and their preparation requires higher temperatures and longer times of exposure to be used. The concentration distribution of foreign ions can only be controlled within narrow limits by adjusting the two parameters.

Similarly to other glasses, also with Simax it may also be expected that the rate of incorporation of foreign ions and their distribution could be controlled within wider limits if a gradient of DC electric voltage were allowed to act alongside the concentration gradient. It was found experimentally that the thickness of layers prepared in this way grows linearly with time, and that the rate of growth increases with increasing current intensity [4]. The character of these relationships implies that the distribution of foreign ions in the layers is homogeneous, that is that there is a sharp boundary between the composition of the surface layer and the deeper layers of the glass. These assumptions are verified in the present study.

EXPERIMENTAL

The thermal exposure of the Simax glass specimens was effected in an experimental arrangement described earlier [3]. It allows specimens in test-tube shape to be used and their interaction with $AgNO_3$ under the effect of constant electric current to be studied. The test-tubes were 140 mm in length, 12 mm in outer diameter, with a wall thickness of 1 mm. The thermal exposure took place at 335 + 5 °C and over the range of 10 to 40 mA of the current (stepped-up by 5 mA). The test-tubes were immersed in $AgNO_3$ melt to a depth of 90 mm. Two different times of exposure ranging from 10 to 45 minutes were chosen for each value.

The thermally exposed specimens were gradually etched in a mixture of 30 ml HF and 0.7 ml HNO_3 (conc.). In the solutions obtained by etching the glass surface, the silver content was established by an ionically selective electrode [3], which was connected by a salt bridge to a saturated calomel electrode. Before the analysis proper, the solution containing the etching products was neutralized by an addition of $CaCO_3$. The Ag content was determined by means of a standard curve. The thickness of the layer removed by etching was measured by a dial gauge with an accuracy of 0.5 μm and checked on the basis of an empirical time dependence of the etching rate. The minimum thickness of the etched-off layer amounted to 2.5 μm.

RESULTS AND DISCUSSION

A series of the concentration profiles of silver in the surface layer of Simax glass is shown in Figs. 1–7. The following findings can be derived from the diagrams:

The expected rectangular profile of Ag concentration arises only at higher DC currents ($I \geq 20$ mA).

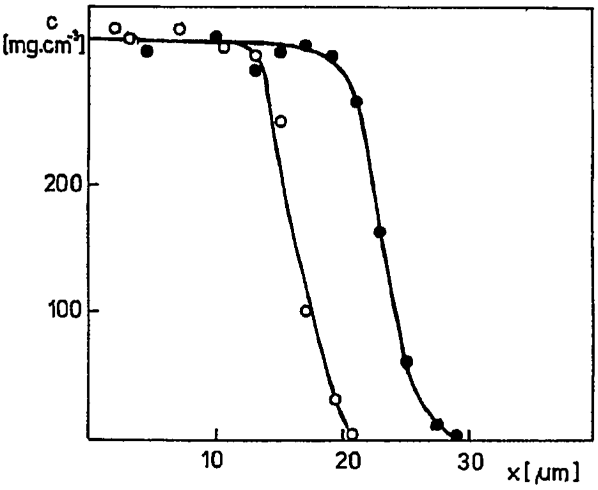

Fig. 1. Distribution of silver concentration (I = 10 mA, t = 335° C, ○ – 25 minutes, ● – 35 minutes).

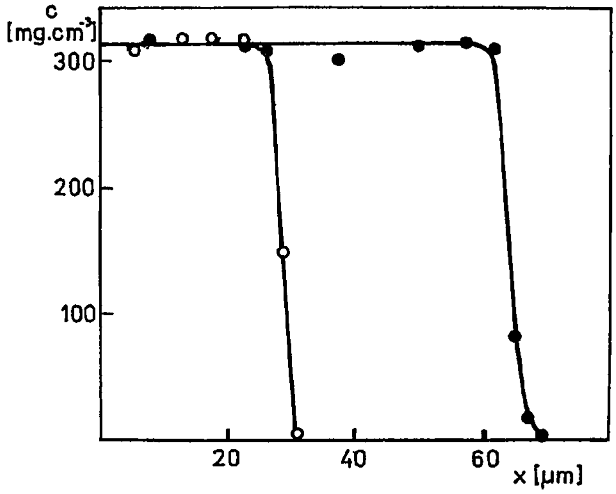

Fig. 3. Distribution of silver concentration (I = 20 mA, t = 335° C, ○ – 20 minutes, ● – 45 minutes).

At lower current values, the main controlling process is probably diffusion and its intensity is commensurable with the flow intensity due to the electric potential gradient. The concentration profile then marks off a constant "saturated" concentration of Ag which is closer to the surface. Below it is a layer in which the concentration of silver decreases down to zero. A transient zone is situated between the two layers, and there the diffusion rate and the rate of ionic migration due to the voltage gradient are commensurable. In general, the concentration profile can be said to consist of three regions illustrated in Fig. 8.

The transient zone gradually diminishes with increasing current intensity, and the deepest zone, where concentration decreases, loses its diffusive character. At the higher values of passing current ($I \geq 20$ mA) the transient zone is almost imperceptible and the diffuse decrease of concentration is replaced by an abrupt one over a short distance. The change in the shape of the concentration profile at the higher current can be explained by the dominating effect of the electric potential gradient which drives the ions at a rate exceeding that due to the concentration gradient. At the moment the potential gradient is switched off, the rectangular distribution of ions, fixed by cooling down the specimen, gives evidence for a frontal advance of ions in the direction from the specimen surface into its interior layers.

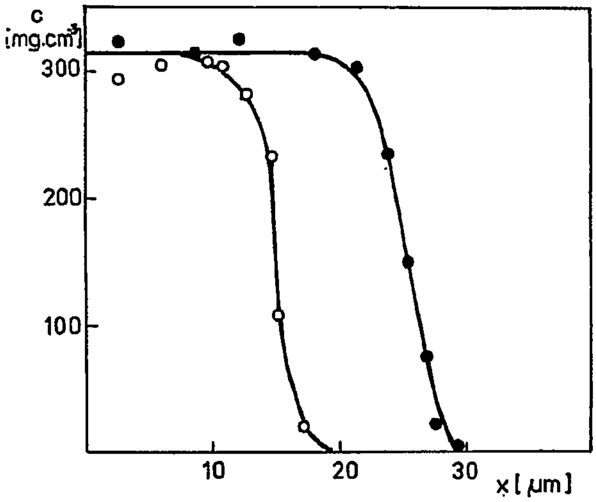

Fig. 2. Distribution of silver concentration (I = 15 mA, t = 335° C, ○ – 15 minutes, ● – 25 minutes).

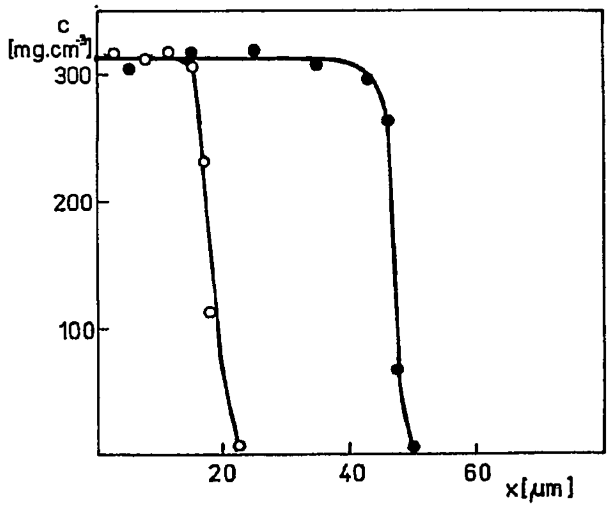

Fig. 4. Distribution of silver concentration (I = 25 mA, t = 335° C, ○ – 20 minutes, ● – 25 minutes).

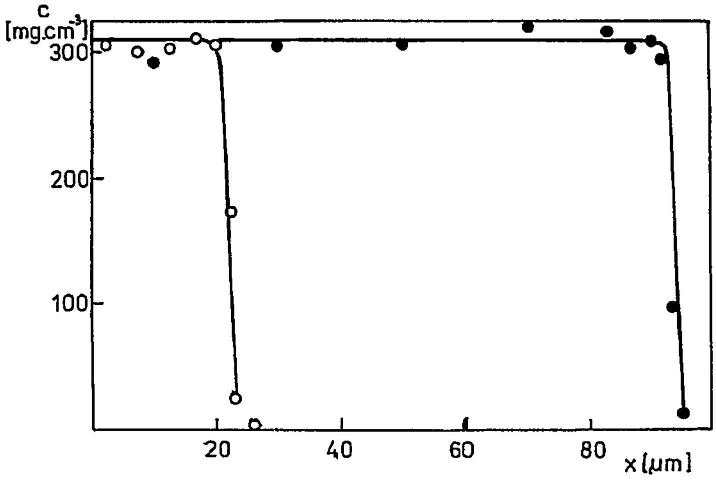

Fig. 5. Distribution of silver concentration (I = 30 mA, t = 335° C, ○ – 10 minutes, ● – 45 minutes).

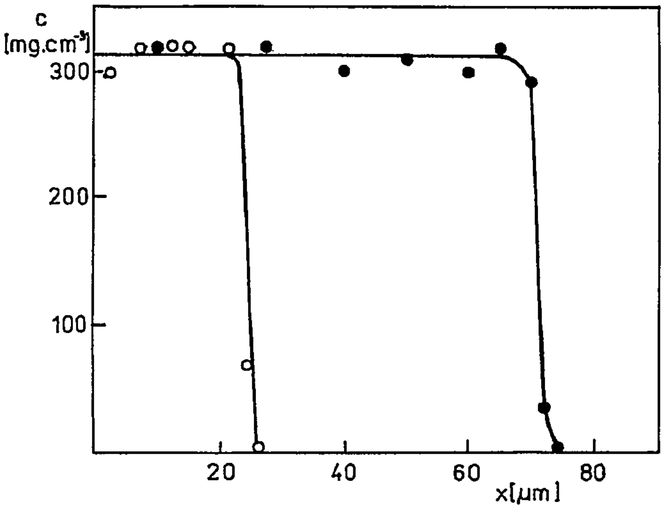

Fig. 6. Distribution of silver concentration (I = 35 mA, t = 335° C, ○ – 10 minutes, ● – 30 minutes).

A mathematical desription of the concentration profiles formed by the simultaneous effects of concentration and electric potential gradients was proposed by Abbou-el-Leil and Copper [5]. For the case of diffusion of Ag ions in glass of the system Na_2O-K_2O-CaO-MgO-Al_2O_3-SiO_2, their procedure was verified in [6]. As indicated by the curves shown in Figs. 1–7, the experimental data are very well described by the equation

$$\frac{C(x,t)}{C_0} = C^* = [1 + \exp(1 - M)(x^* - t^*)]^{-1} \qquad (1)$$

$$x^* = \frac{Ix}{AFC_0D_{\mathrm{Ag}}} \quad \text{and} \quad t^* = \frac{I^2t}{A^2F^2c^20D_{\mathrm{Ag}}} \qquad (2)$$

where the quantities C^*, x^* and t^* have the significance of dimensionless concentration, distance and time, respectively [5]. Parameter M signifies the ratio of the diffusion coefficients of ions taking part in the diffusion process (in our case, D_{Ag} and D_{Na}). The effect of current density I is included in the dimensionless parameters x^* and t^*, defined by equations (2).

In equations (1) and (2): $C(x,t)$ is the actual concentation of Ag in the glass,
C_0 is the total concentration of cations taking part in the diffusion,
A is the area,
x is the distance from the melt-glass interface,

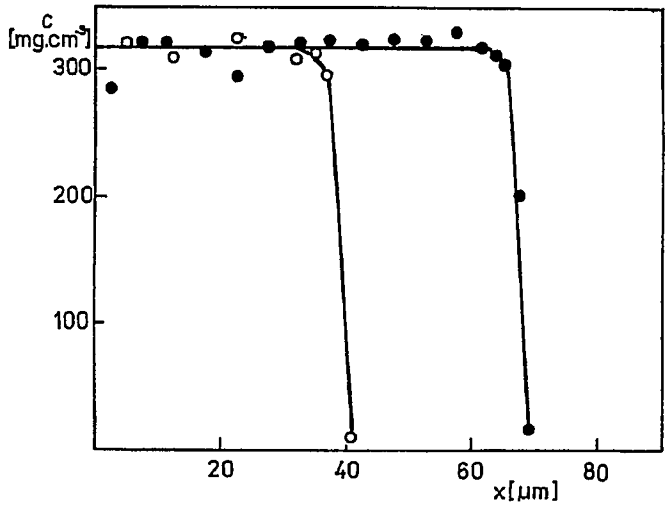

Fig. 7. Distribution of silver concentration (I = 40 mA, t = 335°C, ○ – 15 minutes, ● – 25 minutes).

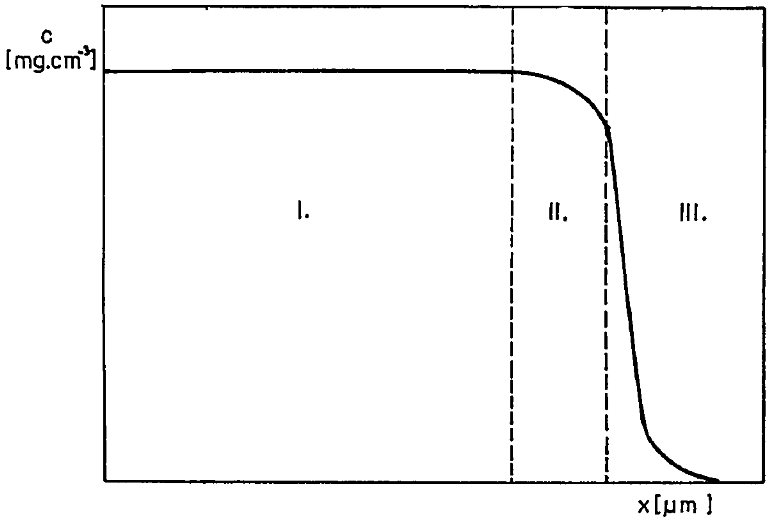

Fig. 8. General shape of the concentration profile of silver (I – zone of constant concentration, II – transient zone, III – zone of diffuse concentration decrease).

t is time,
I is the electric current density,
F is Faraday's constant and
D is the diffusion coefficient.

Calculation of the concentration profile according to equation (1) is relatively cumbersome and requires a number of parameters, which are sometimes difficult to measure, to be known. The complexity of the calculation does not correspond to the well defined shape of the concentration profile, which, particularly for the higher current density values, can be well approximated by the equation

$$C(x,t) = \text{const. for } 0 \le x \le h\,,$$

where h is thickness of the diffusion layer. Only two parameters are involved in this simplified approach to the determination of the concentration profile, namely the concentration of silver and the layer thickness. The constant concentration of silver at the phase boundary can be determined experimentally, or with adequate accuracy put equal to the sum of the concentration of alkali ions in glass. The other procedure assumes complete exchange of silver ions for the alkali ions in the glass. Experience shows that in fact

Table I

Data on the surface layer thickness

I [mA]	μ [nm s^{-1}]	t [min]	h_{theor} [μm]	h_{exp} [μm]	V [%]
10	12	25	20	22	9.09
10	12	35	28	30	6.66
15	19.5	15	18	19	5.26
15	19.5	25	30	29	3.45
20	26	20	32	30	6.67
20	26	45	71	65	9.20
25	32	10	22	20	10.00
25	32	25	52	50	4.00
30	38	10	25	25	0
30	38	45	90	95	5.26
35	42	10	25	26	3.85
35	42	30	76	75	1.33
40	44.5	15	40	40	0
40	44.5	25	70	70	0

the exchange proceeds by only 80–90%.

The thickness of the silver-enriched surface layer can be determined by means of layer thickness growth μ for various time intervals. It has been shown experimentally [4] that the thickness is decribed by the simple equation.

$$h = \mu t . \tag{3}$$

A satisfactory agreement of thickness calculated in this way with the data that can be read from Figs. 1–7 is indicated by Table I. It shows that the relative deviation of surface layer thickness μ, determined according to equation (3), from the corresponding experimental value, does not exceed 10%.

CONCLUSION

Using interaction between Simax glass and $AgNO_3$ melt under the effect of DC at 335°C, surface layers enriched with silver ions were prepared.

The concentration distribution of silver in these surface layers depends on current density. In general, three regions of the concentration profile can be distinguished – that of a constant concentration, a transient region, and that showing a diffusive concentration decrease.

At higher current density levels (above approx. 20 mA), the transient region is already imperceptible and the diffuse decrease of concentration is replaced by its sharp fall over a short distance. The surface layers then exhibit a virtually homogenous distribution of the concentration of silver.

The thickness of the surface layers can be determined on the basis of the speed of advance of the concentration front. As shown by Table I, the values calculated in this way are in a satisfactory agreement with the experimental data.

References

[1] Sjoblom C. A., Anderson J.: Zeitschr. Naturforschung *21a*, 274 (1966).
[2] Doremus R. H.: Phys. Chem. Glasses *9*, 128 (1968).
[3] Maryška M., Matoušek J., Hulínský V.: Silikáty *27*, 289 (1983).
[4] Matoušek J., Maryška M.: Silikáty *36*, 101 (1992).
[5] Abou-el-Leil M., Cooper A. R.: J. Amer. Ceram. Soc. *62*, 390 (1979).
[6] Matoušek J.: Silikáty *29*, 13 (1985).

Translated by K. Němeček

DISTRIBUCE KONCENTRACE STŘÍBRA V POVRCHOVÝCH VRSTVÁCH SKLA SIMAX

JOSEF MATOUŠEK, MARTIN MARYŠKA

Ústav skla a keramiky VŠCHT Praha,
Technická 5, 166 28 Praha 6

Difúzní koeficienty cizích iontů mají ve sklech s menším obsahem alkalických oxidů nízkou hodnotu. Inkorporace cizích iontů do povrchu tohoto typu skel je proto relativně obtížná a nesnadno regulovatelná. Rychlost inkorporace cizích iontů je u skel zpravidla možné regulovat v širších mezích, jestliže vedle gradientu koncentrace působí i gradient stejnosměrného proudu.

U skla Simax o složení 80,4 SiO_2; 13,0 B_2O_3; 2,4 Al_2O_3; 3,6 Na_2O; 0,4 K_2O; 0,06 CaO; 0,04 MgO (hm. %) byla experimentálně sledována interakce s taveninou $AgNO_3$ za působení konstantní hodnoty procházejícího proudu. Tepelná expozice vzorku skla byla provedena za teploty 335°C a v rozsahu proudu 10–40 mA. Distribuce stříbra ve skle byla určená v roztocích vzniklých leptáním skla pomocí iontově selektivní elektrody [3].

Série koncentračních profilů stříbra v povrchové vrstvě skla Simax je znázorněna na obr. 1–7. Průběh koncentačních profilů lze interpretovat v souladu s obr. 8, z něhož vyplývá existence tří oblastí (oblast konstantní koncentrace, přechodná oblast, oblast difúzního poklesu koncentrace). Při vyšších proudových hodnotách ($I \geq 20$ mA) je přechodná oblast nevýrazná a difúzní pokles koncentrace je nahrazen náhlým poklesem koncentrace na velmi krátké vzdálenosti. Povrchové vrstvy se pak vyznačují prakticky homogenním rozdělením koncentrace stříbra.

Tloušťku povrchových vrstev lze určit na základě rychlosti posunu čela frontální distribuce koncentrace. Jak ukazuje tabulka I, jsou takto vypočtené hodnoty v dobrém souladu s experimentálně nalezenými daty.

Obr. 1. Distribuce koncentrace stříbra ($I = 10$ mA, $t = 335$° C, ○ – 25 minut, ● – 35 minut).

Obr. 2. Distribuce koncentrace stříbra ($I = 15$ mA, $t = 335$° C, ○ – 15 minut, ● – 25 minut).

Obr. 3. Distribuce koncentrace stříbra ($I = 20$ mA, $t = 335$° C, ○ – 20 minut, ● – 45 minut).

Obr. 4. Distribuce koncentrace stříbra ($I = 25$ mA, $t = 335$° C, ○ – 20 minut, ● – 25 minut).

Obr. 5. Distribuce koncentrace stříbra ($I = 30$ mA, $t = 335$° C, ○ – 10 minut, ● – 45 minut).

Obr. 6. Distribuce koncentrace stříbra ($I = 35$ mA, $t = 335$° C, ○ – 10 minut, ● – 30 minut).

Obr. 7. Distribuce koncentrace stříbra ($I = 40$ mA, $t = 335$° C, ○ – 15 minut, ● – 25 minut).

Obr. 8. Obecný tvar koncentračního profilu stříbra (I – zóna konstantní koncentrace, II – přechodná oblast, III – zóna difúzního poklesu koncentrace).