

Původní práce

DIFFUSION OF K^+ AND Ag^+ IONS INTO SIMAX GLASS FROM MOLTEN SALTS

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Diffusion of Ag^+ and K^+ ions from $AgNO_3$ and KNO_3 melts into SIMAX glass was studied at 335 °C ($AgNO_3$) and 400—500 °C (KNO_3) using a 6-hour exposure. The concentration profile of silver was determined by the method of gradual etching of layers, and the silver concentration was measured by an ionically selective electrode. The diffusion profiles of potassium were determined by the JXA-5 electron microanalyzer. The diffusion profiles of silver and potassium were used for calculating the interdiffusion coefficients, and the temperature dependence of D_{Na^+/K^+} was established.

INTRODUCTION

Diffusion layers formed on the surface of glasses may considerably affect optical, thermal, chemical, electrical, mechanical and other properties of glasses. In practice, the properties of glasses are adjusted by means of diffusion layers particularly with sheet and container glass. The diffusion layer process has not so far been commercially pursued on glasses designated as type 3.3 according to ISO/TC 48 (Simax, Pyrex, etc.).

The diffusion processes in the Simax glass were dealt with by Novotný [6] who followed gravimetrically the diffusion of K^+ ions from KNO_3 melt at 450—500 °C for periods of 3 to 16 hours. The interdiffusion coefficient values measured on Simax glass can be compared with data from the literature obtained with type 3.3 glasses (cf. eg. [3, 4, 5, 8]). The present study had the aim to determine the interdiffusion coefficients in the interaction of Simax glass with melts of $AgNO_3$ and KNO_3 at 335 °C ($AgNO_3$) and 400—500 °C (KNO_3).

EXPERIMENTAL

The experiments were carried out on tubes of Simax glass supplied by the Kavalier C. C. glassworks. According to [6], the chemical composition of Simax glass in wt. % is as follows: 80.4 SiO_2 , 13 B_2O_3 , 2.4 Al_2O_3 , 3.6 Na_2O , 0.4 K_2O , 0.06 CaO , 0.04 MgO . The tubes had an outside diameter of 12 mm and a wall thickness of 1 mm. Before exposure, they were washed with a dilute detergent solution, then with ethyl alcohol, and dried.

Experiments in $AgNO_3$ melt

The specimen about 140 mm in length, treated as described above, was placed for 6 hours in the $AgNO_3$ melt at 335 ± 5 °C. The temperature was chosen to permit comparison with data from the literature [3, 4]. Following the exposure, the specimen was removed, cooled freely in air and rinsed with water. The concentration

profile of Ag^+ was determined by gradual etching of the glass surface and by determining the silver content in the solution with an ionically selective electrode.

The pretreated specimen was suspended from a platinum holder and immersed in the etching bath (30 ml 6 % HF + 0.7 ml HNO_3 conc.). The bath was agitated by rotating the vessel. After removal from the etching bath, the specimen surface was rinsed with distilled water and dried. Thickness of the etched-off layer was measured with a dial gauge to an accuracy of $\pm 0.5 \mu\text{m}$. The solution of etching products was neutralized with a small excess of CaCO_3 , A.R., transferred into a 50 ml measuring flask and made up to its precise volume. For qualitative determination of silver, the ionic selective silver electrode was connected by a salt bridge with saturated calomel electrode and a standard diagram was employed for evaluation. The concentration of silver expressed in mg Ag per 1 cm^3 of glass was calculated from the known specimen diameter and length, the thickness of the etched-off layer and from the silver concentration [7].

Experiments in KNO_3 melt

The diffusion of K^+ ions from the KNO_3 melt was effected at 400, 425, 450, 475 and $500 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ for a period of 6 hours. The specimens for the individual measurements were prepared in the same way as described above for diffusion from the AgNO_3 melt. Following the time exposure at the given temperature, the specimen was removed from the melt, cooled freely in air and washed with water. Then a cylindrical section about 20 mm in length was cut from the middle part of the specimen, rinsed with water, dried and used for evaluating the concentration profile of potassium by means of the JXA-5 JEOL electron microanalyzer [11, 12]. For this purpose, the cylindrical section of the specimen was cast in epoxy resin; the specimen was then ground with a solid abrasive (22, 10, $5 \mu\text{m}$) and polished with cerium dioxide. After vacuum deposition of an electrically conductive carbon layer the specimen was analyzed by $2 \mu\text{m}$ steps. As this was a polished section through a cylindrical specimen, the actual step amounted to about $0.5 \mu\text{m}$. A precise calculation of the step was carried out separately for each specimen.

RESULTS AND DISCUSSION

The concentration profiles obtained in the manner described above are shown in Figs. 1 through 3. The curves passed through the experimental points represent the

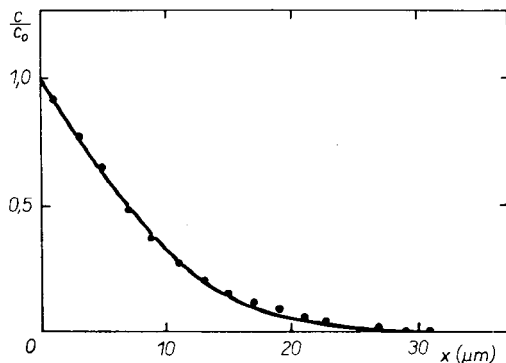


Fig. 1. Concentration profile of silver in Simax glass specimen ($335 \text{ }^\circ\text{C}$, time 6 hours) determined experimentally and calculated from the interdiffusion coefficient established.

theoretical course of relative concentration values, calculated by means of the interdiffusion coefficient values established experimentally. The respective interdiffusion coefficients were obtained from the experimentally determined distribution of K^+ and Ag^+ ions. The diffusion profiles measured were evaluated by means of the relationship (1)

$$\frac{C - C_1}{C_0 - C_1} = \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right), \quad (1)$$

where C is the concentration of the diffusing ion at distance x ,
 C_0 is the surface concentration of the diffusing ion,
 C_1 is the initial concentration of the diffusing ion in glass,
 x is the distance from the surface,
 D is the interdiffusion coefficient,
 t is the time of exposure.

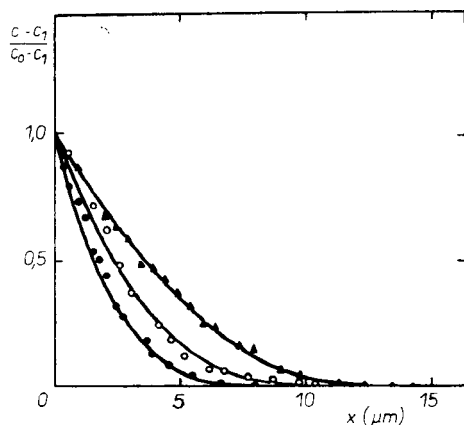


Fig. 2. Concentration profiles of potassium in a Simax glass specimen after 6-hour exposure measured experimentally and calculated from the interdiffusion coefficients established; ● 400 °C; ○ 425 °C; ▲ 450 °C.

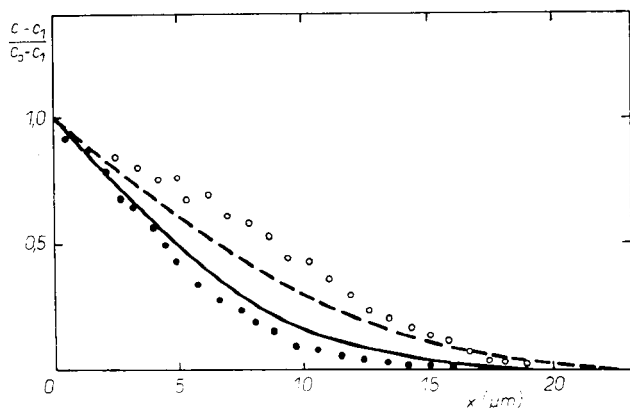


Fig. 3. Concentration profiles of potassium in a Simax glass specimen after 6-hour exposure measured experimentally and calculated from the interdiffusion coefficients established; ● 475 °C; ○ 500 °C.

In the instance when the initial concentration of the diffusing ion in glass $C_1 = 0$ (diffusion from the AgNO_3 melt) relationship (1) acquires the form

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

The relationships are obtained by resolving the 2nd Fick law on the assumption that:

1. the interdiffusion coefficient is independent of the concentration of the diffusing ion;

2. the diffusion involved proceeds from constant source and across a planar interface. This assumption is complied with for tubes with and adequate wall thickness with respect to the diffusion layer thickness, when the latter amounts to max. 1/10th of the tube diameter [2].

An example of the diffusion profile evaluation is given for diffusion from KNO_3 melt at 425°C for a period of 6 hours. The concentration profile was used for calculating the value of function $\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) = \operatorname{erfc}Z$, and the respective Z value was plotted vs. distance x (cf. Fig. 4). The value of \bar{D} was then calculated from

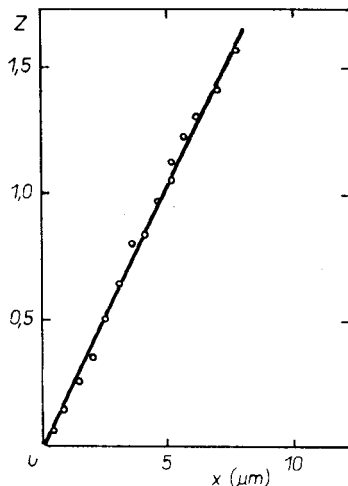


Fig. 4. Dependence of argument Z on the distance from specimen surface x (425°C , KNO_3 melt, 6 hours).

the slope of the relationship $Z = Z(x)$. In the case of diffusion from KNO_3 melt at 475°C and at 500°C , certain deviations from the linear course of the $Z = Z(x)$ function were found, and for this reason the concentration dependence of the interdiffusion coefficient was investigated. The concentration profiles measured were treated by the Boltzman—Matano method and the relationship determined by means of the equation

$$\bar{D}_{C-C_A} = \frac{1}{2t} \frac{dx}{dC} \int_0^{C_A} x^2 dC, \quad (3)$$

where the symbols have the significances defined for the relationships above. The relationship was computed by numerical methods using the SM-3 computer. In both instances the interdiffusion coefficient was found to depend on concentration, as shown in Fig. 5. The mean values of interdiffusion coefficients were used for plotting the temperature dependence of the interdiffusion coefficients. The interdiffusion coefficients obtained were plotted in terms of temperature (cf.

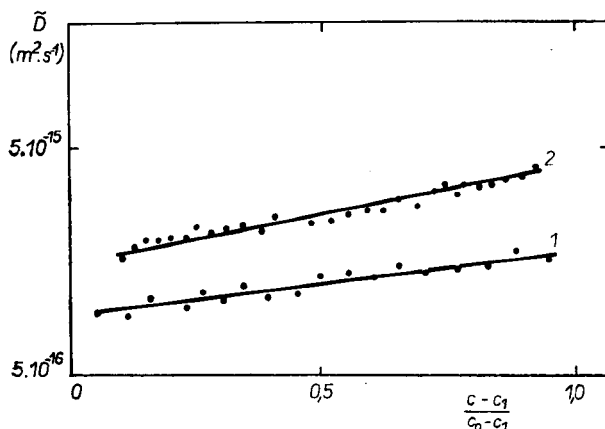


Fig. 5. Dependence of interdiffusion coefficient on concentration of the diffusing ion in Simax glass; straight line 1: KNO_3 melt, $475^\circ C$, 6 hours, straight line 2: KNO_3 melt, $500^\circ C$, 6 hours.

Fig. 6, hollow rings) and the temperature dependence of the interdiffusion coefficient was determined by the least squares method according to the equation

$$\tilde{D} = D_0 \exp(-E/RT), \quad (4)$$

where D_0 is the frequency factor [$m^2 s^{-1}$],

E is the activation energy of diffusion [$J mole^{-1}$],

R is the gas constant [$J mole^{-1} K^{-1}$],

T is thermodynamic temperature [K].

From the temperature dependence obtained (line 2 in Fig. 6), which for the temperature interval of $400 \div 500^\circ C$ has the form

$$\tilde{D} = 1.267 \times 10^{-7} \exp(-115\,020/RT) \quad [m^2 s^{-1}], \quad (5)$$

the interdiffusion coefficients for potassium diffusion were calculated inversely and used for plotting the theoretical course of concentration profiles (Figs. 2 and 3). Fig. 2 demonstrates a very satisfactory agreement between the measured and the calculated concentration profiles for potassium. The deviations arising in Fig. 3 are probably due to a concentration dependence of the interdiffusion coefficient. In the case of diffusion from $AgNO_3$ melt, the plotting of the theoretical concentration profile $C = C(x)$ was based on the interdiffusion coefficient obtained from the relationship $Z = Z(x)$, the value of which for $335^\circ C$ is $2.4 \times 10^{-15} [m^2 s^{-1}]$. Fig. 1 again shows a very good agreement between the measured and the computed concentration profiles. The results can be compared with the values obtained on Pyrex glass which has a similar chemical composition (Table I).

Table I
Composition of glasses Simax [6] and Pyrex [5]
in wt. %

Component	Simax	Pyrex 7740
SiO ₂	80.4	81
B ₂ O ₃	13	13
Al ₂ O ₃	2.4	2
Na ₂ O	3.6	4
K ₂ O	0.4	0.5
CaO	0.06	
MgO	0.04	

Diffusion of silver into Pyrex glass from AgNO₃ melts was studied by Sjöblom and Anderson [3] and Doremus [4]. The values of interdiffusion coefficients obtained by these authors, i.e. 2.57×10^{-15} [m² s⁻¹] [3] and 3×10^{-15} [m² s⁻¹] [4] are in a satisfactory agreement with the value 2.4×10^{-15} [m² s⁻¹] determined in the present study. Measurement of the diffusion of silver into Simax glass has at the same time served as a check of the method before further measurements.

Diffusion of potassium from KNO₃ melt had already been studied earlier both on Pyrex glass [5, 8] and with Simax glass [6]. The measurements carried out on Simax glass were of orientation character only and the interdiffusion coefficients were determined from the difference in the specimen weight before and after the ion exchange. This method may involve a considerable error and need not always lead to precise results. The data given in the literature for Pyrex glass are not quite consistent with those for Simax glass. Studies [6, 8] also involve the time dependence of interdiffusion coefficients. Whereas according to Novotný [6] the interdiffusion coefficient increases in terms of time (from 2.7×10^{-16} [m² s⁻¹] at 3-hour exposure up to 1.7×10^{-15} [m² s⁻¹] at 16-hour exposure at 450 °C), according to Morris [8] it decreases with time (from 5.5×10^{-16} [m² s⁻¹] at 1-hour exposure down to 1×10^{-16} [m² s⁻¹] at 2.187-hour exposure, 400 °C). According to [8] this time dependence decreases with increasing temperature, and none has been found at 600 °C. For Pyrex glass [5] the temperature dependence of the interdiffusion coefficient for diffusion for KNO₃ melts is described for the 350 to 450 °C temperature range by the equation

$$D = 8.2 \times 10^{-8} \exp(-108\,719/RT) \quad [\text{m}^2 \text{s}^{-1}], \quad (6)$$

where the significance and dimensions of units are the same as in equation (4). The data presented in the study indicate that the values of activation energy for potassium diffusion in Pyrex and Simax glasses are very close. A graphic comparison of equations (5) and (6), the data by Novotný [6] and of the experimentally established points is shown in Fig. 6. Compared to Pyrex glass (line 1) the interdiffusion coefficients for Simax glass (line 2) have roughly half the value, which may be due to deviations in the composition of the two glasses, particularly as regards the Na₂O content which is somehow higher in Pyrex glass. The interdiffusion coefficients may likewise be considerably affected by the thermal history of the specimen. Separation leads to the formation of two phases with considerably differing chemical composition; the silicate phase contains 0.4 wt. % Na₂O and

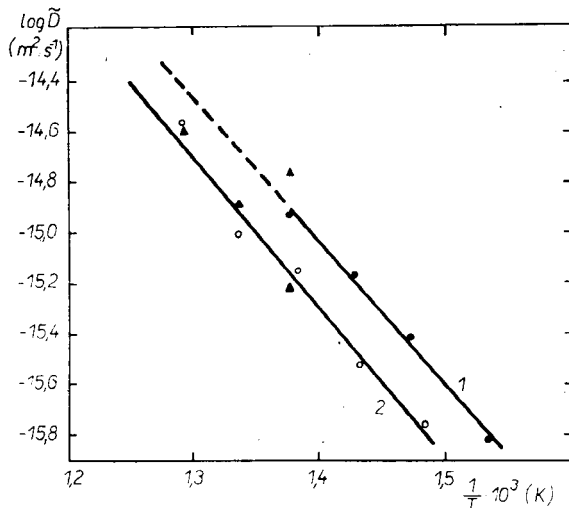


Fig. 6. Temperature dependence of the logarithm of interdiffusion coefficient; 1 — equation (6) according to [5], Pyrex glass, \circ — experimental points according to [5]. 2 — equation (5) — the present study, Simax glass, \circ — experimental points — the present study, \blacktriangle — experimental points according to [6].

the boric phase contains 26.1 wt. % Na_2O [8]. Then the ions in the phase enriched in alkali ions start to move at a higher rate, so that different results may be obtained. In contrast to this, in the silicate phases the diffusion of ions may proceed at a substantially lower rate. The values measured therefore depend on the comparative content of the two separated phases, and on their distribution. The concentration dependence of the interdiffusion coefficient at 475 °C and at 500 °C (Fig. 5) has a linear course, in contrast to glasses with a high content of alkali ions [10,11]; this linear course is probably due to a low concentration of alkali ions in glass. At 475 °C the interdiffusion coefficient value changes from 7.5×10^{-16} [$m^2 s^{-1}$] to 9.5×10^{-16} [$m^2 s^{-1}$] and at 500 °C this change is from 9.5×10^{-16} [$m^2 s^{-1}$] to 4.3×10^{-15} [$m^2 s^{-1}$]. Study [8] describes the concentration dependence of the interdiffusion coefficient for the $K^+ - Na^+$ exchange in Pyrex glass at 400 °C. This dependence was found to be approximately linear at exposure times longer than 200 hours; at shorter times of exposure the dependence is similar to that of glasses with a higher content of alkali ion, but the difference between the maximum and the minimum value is not so pronounced; $\tilde{D}_{min} = 3.2 \times 10^{-16}$ [$m^2 s^{-1}$], $\tilde{D}_{max} = 5.5 \times 10^{-16}$ [$m^2 s^{-1}$] at 1-hour exposure. At longer terms of exposure the dependence of \tilde{D} on concentration becomes less distinct.

CONCLUSION

Interdiffusion coefficients were measured during interaction of Simax glass with melts of $AgNO_3$ and KNO_3 .

In the case of $AgNO_3$ the diffusion proceeded at 335 °C, and the interdiffusion coefficient established, $\tilde{D} = 2.4 \times 10^{-15}$ [$m^2 s^{-1}$] is in a satisfactory agreement with the data from the literature for Pyrex glass.

In the instance of KNO_3 the diffusion was examined at 400–500 °C and the interdiffusion coefficient was found to have the following temperature dependence:

$$\bar{D} = 1.267 \times 10^{-7} \exp(-115\,020/RT) \quad [\text{m}^2 \text{s}^{-1}].$$

The diffusion activation energy value established is in a good agreement with the value of 108 719 [J mole⁻¹] for Pyrex glass [5].

At 475 and 500 °C, the interdiffusion coefficient was found to be linearly dependent on the concentration of the diffusing ion. The most significant concentration dependence occurs at 500 °C, where the interdiffusion coefficient values increase with concentration from approx. 9.5×10^{-16} [m² s⁻¹] up to 4.3×10^{-15} [m² s⁻¹].

References

- [1] Crank J.: *The Mathematics of Diffusion*; Clarendon Press, Oxford 1975.
- [2] Zhuravlev G. I., Jevstishenko V. S., Kuznetsov A. I., Golova E. P.: *Fizika i chimija stekla*, 7, 414 (1981).
- [3] Sjöblom C. A., Andersson J.: *Zeitschrift für Naturforschung* 21a, 274 (1966).
- [4] Doremus R. H.: *Physics and Chemistry of Glasses* 9, 128 (1968).
- [5] Iino A., Nakamura H., Mizuike A.: *Nippon Kagaku Kaishi*, 9, 1324 (1977).
- [6] Novotný V.: Unpublished Research Report DIFUSE, 1975, State Glass Research Institute, Hradec Králové 1975.
- [7] Beran J.: Diffusion layers in Glass Simax, (in Czech), Graduate's Thesis, Department of the Technology of Silicates, Institute of Chemical Technology Prague 1982.
- [8] Morris A. P., Dosdale T., Knott P.: *Non-Crystalline Solids*, 38–39, 539 (1980).
- [9] Matoušek J., Blažek J.: *Silikáty* 23, 193 (1979).
- [10] Matoušek J., Hlaváček E.: *Silikáty* 23, 203 (1979).
- [11] Hulínský V. et al.: *The Methods of Electron Microanalysis and Microscopy in the Research of Glasses*, (in Czech), Unpublished Research Report IV-5-3/6, Department of the Technology Prague 1978.
- [12] Vašková L., Hulínský V., Drncová E.: *Silikáty* 20, 289 (1976).

ДИФФУЗИЯ ИОНОВ K^+ И Ag^+ В СТЕКЛО SIMAX ИЗ РАСПЛАВОВ СОЛЕЙ

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Исследовали диффузию ионов Ag^+ и K^+ из расплавов AgNO_3 и KNO_3 в стекле Simax при температурах 335 °C (AgNO_3) и 400–500 °C (KNO_3) при выдержке 6 часов. Концентрационный профиль серебра определяли постепенным травлением поверхностного слоя и в образовавшемся растворе устанавливали концентрацию серебра при помощи ионно-селективного серебряного электрода. Концентрационные профили калия устанавливали с помощью электронного микросонда Ф J XA-5.

На основании концентрационных профилей устанавливали соответствующие интердиффузионные коэффициенты с помощью отношения (2) в случае диффузии из расплава AgNO_3 и с помощью отношения (1) в случае диффузии из расплава KNO_3 . Из таким образом полученных интердиффузионных коэффициентов обратно рассчитывали концентрационные профили соответствующих ионов и сопоставляли их с измеренными (см. рис. 1–3).

В случае диффузии из расплава KNO_3 при температурах 475 °C и 500 °C устанавливали отклонения между рассчитанными и измеренными концентрационными профилями и поэтому концентрационную зависимость интердиффузионного коэффициента исследовали с помощью метода Больцмана—Матана. Полученные зависимости приводятся на рис. 5. Для диффузии из расплава KNO_3 установили температурную зависимость

интердиффузионного коэффициента согласно уравнению (4) в виде $\tilde{D} = 1,267 \cdot 10^{-7}$ экс. ($-115\ 020/RT$) [$m^2 \cdot s^{-1}$]. Таким образом полученная зависимость весьма близка отношению, полученному для стекла Pyrex.

- Рис. 1. Концентрационный профиль серебра в пробе стекла Simax (335 °C, выдержка 6 часов), измеренный экспериментальным путем и рассчитанный из установленного интердиффузионного коэффициента.
- Рис. 2. Концентрационные профили калия в пробе стекла Simax после выдержки 6 часов, измеренные экспериментальным путем и рассчитанные из установленных интердиффузионных коэффициентов; ● 400 °C, ○ 425 °C, ▲ 450 °C.
- Рис. 3. Концентрационные профили калия в пробе стекла Simax после выдержки 6 часов измеренные экспериментальным путем и рассчитанные из интердиффузионных коэффициентов; ● 475 °C; ○ 500 °C.
- Рис. 4. Зависимость аргумента Z от расстояния от поверхности пробы x (425 °C, расплав KNO_3 , выдержка 6 часов).
- Рис. 5. Зависимость интердиффузионного коэффициента от концентрации диффундирующего иона в стекле Simax; прямая 1: расплав KNO_3 , 475 °C, выдержка 6 часов, прямая 2: расплав KNO_3 , 500 °C, выдержка 6 часов.
- Рис. 6. Зависимость логаритма интердиффузионного коэффициента от температуры 1 — отношение (6) согласно [5], стекло Pyrex, ○ — экспериментальные точки согласно [5], 2 — отношение (5) — предлагаемая работа, стекло Simax, ○ — экспериментальные точки — предлагаемая работа, ▲ — экспериментальные точки согласно [6].

DIFÚZE IONTŮ K^+ a Ag^+ DO SKLA SIMAX Z TAVENIN SOLÍ

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Byla sledována difúze iontů Ag^+ a K^+ z tavenin $AgNO_3$ a KNO_3 do skla Simax při teplotách 335 °C ($AgNO_3$) a 400—500 °C (KNO_3) při časové expozici 6 hodin. Koncentrační profil stříbra byl určen postupným odleptáváním povrchové vrstvy a ve vzniklém roztoku byla stanovena koncentrace stříbra iontově selektivní stříbrnou elektrodou. Koncentrační profily draslíku byly stanoveny na elektronové mikrosondě JXA-5.

Ze získaných koncentračních profilů byly vyhodnocovány příslušné interdifúzní koeficienty pomocí vztahu (2) v případě difúze z taveniny $AgNO_3$ a pomocí vztahu (1) v případě difúze z taveniny KNO_3 . Z takto získaných interdifúzních koeficientů byly zpětně vypočítány koncentrační profily příslušných iontů a porovnány s naměřenými (obr. 1—3).

V případě difúze z taveniny KNO_3 při teplotách 475 °C a 500 °C byly zjištěny odchylky mezi vypočítanými a naměřenými koncentračními profily, a proto byla zkoumána koncentrační závislost interdifúzního koeficientu metodou Boltzmanovou—Matanovou. Získané závislosti ukazují obrázek 5. Pro difúzi z taveniny KNO_3 byla stanovena teplotní závislost interdifúzního koeficientu podle vztahu (4) ve tvaru $\tilde{D} = 1,267 \cdot 10^{-7} \exp(-115\ 020/RT)$ [$m^2 \cdot s^{-1}$]. Takto získaná závislost je velice blízká vztahu získanému pro sklo Pyrex.

- Obr. 1. Koncentrační profil stříbra ve vzorku skla Simax (335 °C, čas 6 hodin) naměřený experimentálně a vypočítaný z určeného interdifúzního koeficientu.
- Obr. 2. Koncentrační profily draslíku ve vzorku skla Simax po šestihodinové expozici naměřené experimentálně a vypočítané z určených interdifúzních koeficientů; ● 400 °C; ○ 425 °C; ▲ 450 °C.
- Obr. 3. Koncentrační profily draslíku ve vzorku skla Simax po šestihodinové expozici naměřené experimentálně a vypočítané z určených interdifúzních koeficientů; ● 475 °C; ○ 500 °C.
- Obr. 4. Závislost argumentu Z na vzdálenosti od povrchu vzorku x (425 °C, tavenina KNO_3 , 6 hodin).
- Obr. 5. Závislost interdifúzního koeficientu na koncentraci difundujícího iontu ve skle Simax; přímlka 1: tavenina KNO_3 , 475 °C, 6 hodin, přímlka 2: tavenina KNO_3 , 500 °C, 6 hodin.
- Obr. 6. Závislost logaritmu interdifúzního koeficientu na teplotě; 1 — vztah (6) podle [5] sklo Pyrex, ● — experimentální body podle [5], 2 — vztah (5) — tato práce sklo Simax, ○ — experimentální body — tato práce, ▲ — experimentální body podle [6].