The Effect of Surface Layers Prepared by Sol-Gel Method on Glass Corrosion

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Introduction

Different surface modification methods are used in order to improve the chemical resistance of silicate glasses, e.g. dealkalization of glass surface or preparing of protective layers using CVD, PVD and sol-gel method. The sol-gel method has the certain advantages compared to other technologies: low process cost, low temperature of heat treatment, high uniformity of film and wide possibility to vary film properties by changing the composition of the initial solution. Layers prepared using sol-gel method may improve not only chemical but optical and mechanical properties of original material, too. The aim of present study was to estimate the effect of surface layers based on silicon dioxide and titanium dioxide on glass corrosion and to describe kinetics of corrosion with the aid of a mathematical model.

Experimental

The experiments were carried out on the reference samples (microscope slides) and on the samples with TiO_2 and SiO_2 surface layers. The layers were prepared on soda-lime microscope slides. Before application, the substrate was cleaned with detergent, washed in deionized water, rinsed with ethanol and then dried in a drying oven. The sol of titanium dioxide and silicon dioxide were prepared. Tetra-n-butyl orthotitanate, isopropyl alcohol and deionized water were the starting compounds for the preparation of TiO_2 layers [1]. Hydrochloric acid or acetic acid was added as the catalyst. Tetraethoxysilane, isopropyl alcohol, deionized water and hydrochloric acid were starting compounds for the preparation of SiO_2 films [2]. A sol was obtained after mixing of starting solutions in the electromagnetic stirrer. The layers were applied on the glass substrate by dip-coating method. The glass substrate was

dipped into the solution for a period of 30 second, pulled up at constant pull rate of 6 cm/min, dried in a drying oven for 30 minutes at 60°C, followed by firing at 450°C or 550°C for 45 minutes. Transparent TiO_2 and SiO_2 films were obtained. The thickness of prepared layer was measured by profilometer.

Static corrosion tests were performed at temperature 60°C in unbuffered solution with initial value $pH_{t=0}$ =10.5 and in buffered solutions with pH values 10.5 and 7.7. The chemical durability of the specimens was established by determining the total content of Si in the leachate which was determined by spectrophotometer.

Results and discussion

The time dependence of Si amount during corrosion in unbuffered solution with initial pH value 10.5 and the time dependence of pH are plotted on fig. 1 and fig. 2, respectively.
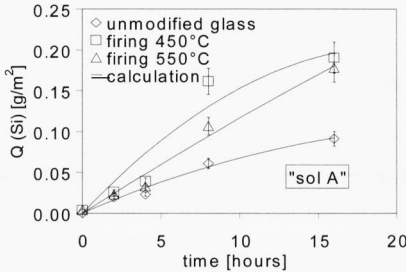

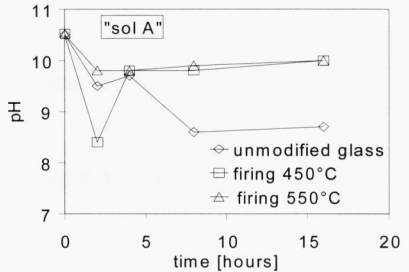Fig.1. The time dependence of Si solution concentration in unbuffered solution

Fig. 2. pH of solution versus time of corrosion

The results given in figure 1 show, that the specimens with TiO_2 layer dissolve more rapidly compared to unmodified glass. These results can be explained by pH changes during the test. While pH value of the reference samples decreased after several hours of corrosion from 10.5 to 8.6, pH of the samples with TiO_2 layer became stable at pH value 10 (fig. 2). This different change of pH can be caused by sodium ions diffusion from glass into deposited film during firing. Subsequently, these ions diffuse into corrosion solution increasing its pH. Following non-linear equation was used to fit experimental time dependence of Q_{Si} [3]:

$$Q_{Si} = \frac{B}{k}\left[1 - \exp(-kt)\right] + wt \qquad (1)$$

where B, k and w are empirical constants.

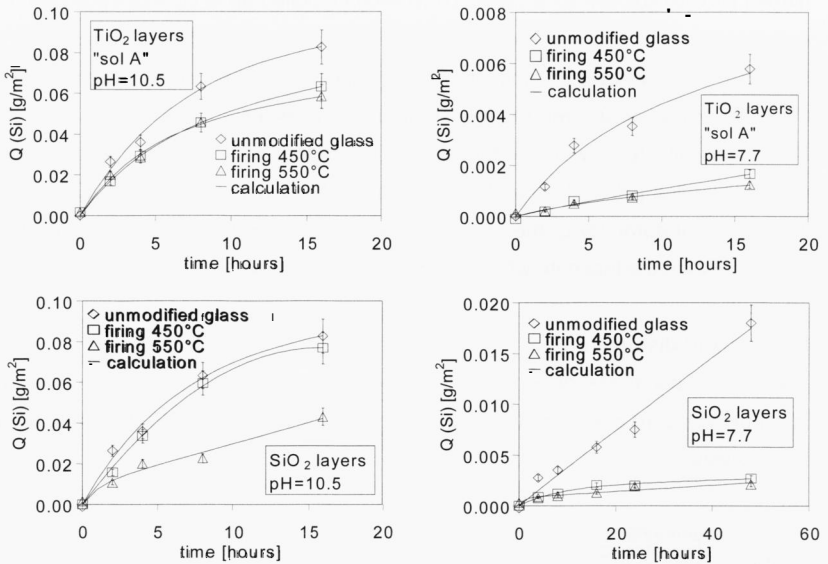Glastech. Ber. Glass. Sci. Technol. 77 C (2004)

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Fig.3. The time dependence of Si solution concentration in buffered solution

Figure 3 shows the time dependence of silicon amount during exposure in buffered solutions with pH values 10.5 and 7.7. Both TiO_2 and SiO_2 layers decrease glass dissolution into buffered solutions. The increased temperature of firing decrease glass dissolution rate in the case of SiO_2 layers only. Diffusion coefficients, which describe transport of surface reaction products through the deposited layer, were calculated. Provided that control mechanism is surface reaction, unmodified glass dissolves according to equation [4]:

$$\frac{dQ_{Si}}{dt} = k^+ (c_s - c)$$ (2)

where k^+ is rate constant of surface reaction, c_s and c are saturated and actual Si concentration in solution, respectively. Provided that surface reaction is followed by diffusion of product through layer with constant thickness, we can describe the dissolution of glass with deposited layer by following equation [4]:

$$\frac{dQ_{Si}}{dt} = \frac{k^+ \dfrac{D}{h}}{k^+ + \dfrac{D}{h}}(c_s - c)$$ (3)

where D is diffusion coefficient of surface reaction products in protective layer and h is layer thickness. At $t \to 0$ is Si solution concentration $c \to 0$. The value of k^+ was then

computed from equation (2) using the experimental initial rate of dissolution of unmodified glass and c_s value (c_s=192 g.m^{-3} at pH=10.5 and c_s=110 g.m^{-3} at pH=7.7) obtained from PHREEQC code [5]. Then, using measured thicknesses of both TiO$_2$ and SiO$_2$ layer (300 nm and 95 nm, respectively) the D value from equation (3) was obtained using the initial rate of dissolution of specimen with layers.

Tab.I. Surface reaction rate constant a diffusion coefficients evaluated from experimental data

pH	k^+ [m/s]	D [m^2/s]	
		TiO$_2$ layers	SiO$_2$ layers
7.7	$1.5 \cdot 10^{-9}$	$1.5 \cdot 10^{-16}$	$1.7 \cdot 10^{-16}$
10.5	$1.9 \cdot 10^{-8}$	$7.1 \cdot 10^{-15}$	$5.1 \cdot 10^{-15}$

The dependence of D on pH value and similar values of D for different layers suggests that the surface reaction products are transported in aqueous phase through the pore system rather than through the layer itself.

Conclusions

Both TiO$_2$ and SiO$_2$ layers decrease glass dissolution into buffered solutions. Control mechanism of dissolution is probably transport of surface reaction products through the porous system in deposited layer. In unbuffered solutions, the leaching of Na$^+$ ions from the layers and consequent pH changes exceeds their protective function.

References

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2. Jiřičková J.: PhD thesis, ICT Prague, 2004

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