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Effect of the Silica Sol–Gel Coatings on the Properties of Glass Substrate

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Abstract: Strengthening of the glass substrate with silica sol-gel coatings was investigated. Sol–gel silica coating microstructure (is related to the degree of substrate strengthening), as it is known depends on the silica sol structure. In order to produce different microstructures of the silica coating, a variety of silica sols were prepared starting from TEOS and changing the water and solvent content, catalyst type and concentration, at room temperature. Carefully prepared glass surfaces were coated with silica sol using a dipping technique, with constant withdrawing rate (all physical parameters of the deposition were constant, since they can additionally change the coating microstructure). After specific heat treatment of the samples, the modulus of rupture was calculated using the measured flexural strength data. The degree of the substrate strengthening depends on the quantity of water used for the sol preparation, coating sol pH, state of the substrate surface and the degree of the coating bonding to the substrate (all mentioned parameters are discussed as to how they effect the silica sol structure). Results showed that strengthening of the glass substrate is effected by the microstructure of the silica coating. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Sol–gel derived coating is one of the most promising applications of sol–gel techniques, since coating can be applied on various substrates, such as metals, glass and ceramics, and without expensive equipment. Besides, it can improve mechanical, thermal, optical, protective and electrical properties of the materials.[1–3] The surface of solid bodies represents a simple target for the application of economic coatings . This is much easier to accomplish than to design new bulk materials for specific applications.[4,5] Today sol–gel coatings are being studied for diverse range of applications.[6,7]

The strength of brittle materials is one of the bulk properties, which is largely controlled by surface conditions. Recent studies[8–11] have shown that strength of the brittle materials can be improved by sol–gel coatings. The Ulhman's research group[7,8] reported that densified coatings increase strength of silica glass with silica sol–gel coating up to 130%. They have derived the model of the sol–gel strengthening of glass, based on: the filling-in surface flaws, blunting crack tips, adding a compressive stress to the surface; protecting the material from fatigue, or by any combination of the above.[8] The model accounts for temperature dependence of strengthening. Presence of significant residual tensile stress in sol–gel strengthened material is also indicated.[8]

The subject of this paper is to study the strengthening of the alkali silicate glass by silica sol–gel coating. The strengthening of the alkali silica glass plates were studied as a function of the silica sol–gel coating microstructure which in turn is determined by silica gel microstructures. The microstructure of the silica gel derived coating depends on the chemical parameters of the sol preparation (water content and sol pH values) and physical parameters of the dip coating (coating sol viscosity, the state of substrate surface and the coating thickness). The influence of the substrate surface flaws on the strengthening was studied by inducing the flaws with Vickers indentation. The

characterization of the degree of strengthening was performed by measuring bending strength and calculating the rupture values.

2 EXPERIMENTAL

As is well known[1] the silica sol structure determines the final silica coating microstructure and its properties. In order to study the influence of the silica coating microstructure on the glass substrate strengthening, silica coating sols, having different structure were prepared. As a starting material for silica sol preparation: tetraethylorthosilicate (the samples are noted by letter C, Table 1) and commercial colloidal silica sol, Ludox; (the sample is noted by letter L, Table 1) were used.

The compositions of silica coating sols which are prepared in this experiment are presented in Table 1. The first four silica coating samples, Table 1, were prepared by partially hydrolyzing tetraethylorthosilicate (TEOS, produced by FLUKA), with one mole of water per one mole of TEOS in half of the total amount of ethanol required. A small amount of catalyst (HCl or NH_4OH) was added into the water. After mixing for about 1 h, the rest of the ethanol and water with catalyst (in order to get pH values given in Table 1) was added into this mixture, as shown in Fig. 1. The figure shows schematic diagram for preparation of silica sol–gel coating. The amount of water was added in order to reach the R values (R is mole ratio of water per mole of TEOS) given in Table 1. The mole ratio of added ethanol per mole of TEOS was kept constant in all experiments, being about 5. For spinnable silica sol R values should be about 2,[1] but in our experiments we used even more water (Table 1). For about 1 h silica sols were vigorously stirred at room temperature. The silica sols for coatings were diluted with ethanol just before coating, in order to adjust viscosity of the sol to be optimal for the coating.

When Ludox (Ludox AS 40, DU PONT), as a colloidal silica sol, was used in the experiments only pH values of the sol were adjusted using catalyst (Table 1).

Table 1. The compositions of the silica coating sols

Sample notation	Mole ratio H_2O/TEOS=R	pH values
$2C_1$	2	1
$4C_1$	4	1
$10C_1$	10	1
$2C_8$	2	8.5
L_8	—	8.5

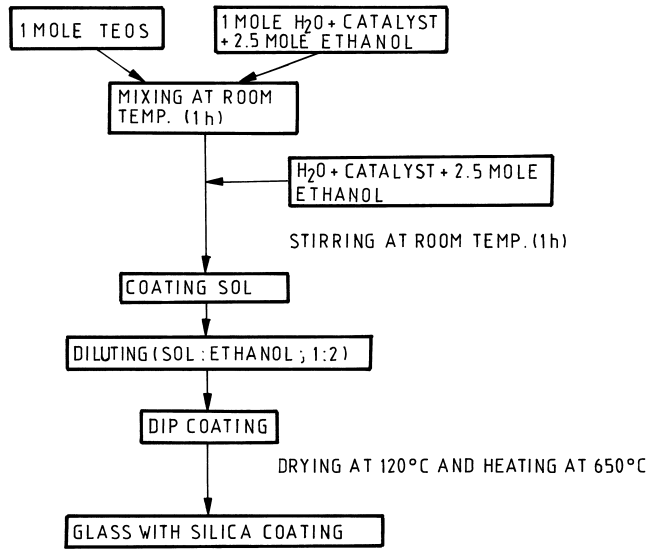

Fig. 1. Scheme for processing of sol–gel silica coating.

Alkali silica glass plates, dimension 26×15×1 mm, were used as the substrate materials for experiments. Immediately before deposition, substrates were ultrasonically cleaned successively in methylene chloride and acetone and then wiped with ethanol.

In order to study the influence of the silica substrate surface state on the strengthening of silica plates the flaws were induced by Vickers indentations. Using a Vickers indenter each plate was indented once in the center with a load of 50 N before coating. The surface of these substrates were carefully examined by optical microscope, before and after Vickers indentation.

Dip technique was used for coating. Drawing rate of substrate from coating sol, was 6 cm min^{-1}. After coating, samples were dried for 15 min at 120°C and after that, heated up to 650°C for 10 min.

The coating sols were characterised using absorption IR spectrometer using KBr pellets, (Perkin–Elmer 399). The silica coating microstructures were examined by scanning electron microscope (SEM) (JEOL 35) on the fresh fractured surface coated with gold. Bending strength was measured by Instron 1122 equipment. The samples were broken in 4-point bending using a crosshead speed of 5 mm min^{-1}. Modulus of rupture, MOR, was calculated using bending test values.[12]

3 RESULTS AND DISCUSSION

3.1 Sol characterisation

Since the idea was to relate to sol structure and final coating properties, sols were prepared, with expectation to have different structures.[1] The sol

structure before coating was checked by using IR spectra. The coating sols IR spectra are shown in Fig. 2. As is obvious in Fig. 2, coating sols do have different structures, as was our intention in the designing of experiments. The bends noted by: S, D, R (1089 cm^{-1}, 800 cm^{-1} and about 450 cm^{-1}, respectively)[13] are characteristic for different modes of the Si–O vibrations. They are different in intensity and shape for the samples $2C_1$, $4C_4$., $10C_1$. These sols with same pH values, being 1, but different R, being from 2 to 10, have a more or less silica chain branched structure as a consequence of the quantity of water used for hydrolysis.[1,14] That different degree of silica chain branching has influence on the Si–O vibration modes, S, R, D, as can be seen in Fig. 2. Ludox, L_8 particulate sol, and particulate sol which we prepared, $2C_8$, also have different IR spectra (Fig. 2). The bend at 980 cm^{-1} is characteristic for the Si–O nonbridging oxygen vibration. This bend is not characteristic for particulate sols (L_8 and $2C_8$) but only for silica chain structure, indicating the degree of branching (the samples $2C_1$, $4C_1$, $10C_1$). This bend is the most pronounced for the sol $2C_1$ which means that sol has the highest concentration of the OH groups, in respect to the other sols. Branched chain like silica sols ($4C_1$ and $10C_1$) have a lot of bonded water (bends at 3600 cm^{-1} and 1620 cm^{-1}) but particulate one does not contain bonded water (this result is not shown in Fig. 2). This difference in quantity of bonded water is an important parameter for the final density/porosity of the coating. The density/porosity of the coating strongly depends on the size of the precursor species in the sol.[8]

3.2 The coating effect on the glass substrate strengthening

3.2.1 Coatings on the flawless glass surface

The intrinsic strength of flawless glass under inert conditions is very high (about 14 GPa).[15] A small crack at glass surface causes a dramatic decrease in the glass strength, because they initiate crack propagation under modest tensile stress. Even nanoscale surface imperfections caused by hydrolysis of Si–O–Si bonds at the glass surface can serve to propagate fractures under stress and chemically reactive conditions (especially in the presence of water). The measured rupture strength of the alkali silica glass substrate, which was used in all experiments was about 120 MPa. Silica sol–gel coating applied to the glass surface could heal surface damages, potentially form compressive layers which strengthen glass plate and protect it. Besides, the glass substrate strengthening with silica sol–gel coating depends on the coating microstructure too, but in a rather complex manner.[7–9]

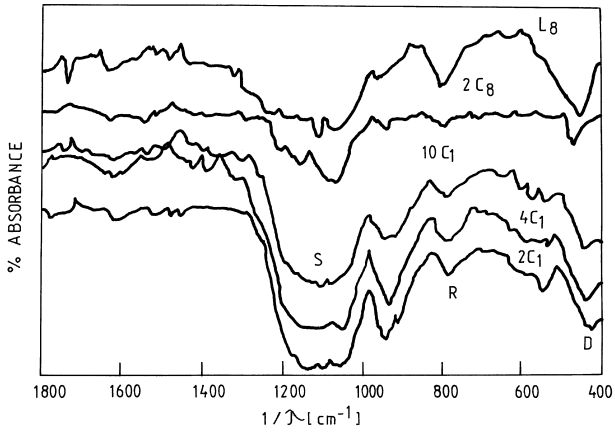

Fig. 2. IR spectra of different coating sols.

The resulting silica coating microstructures (after heating) are related to the silica sol structures and effect on the strengthening glass substrate. Glass substrates which were used in experiments, have a coefficient of thermal expansion of CTE $\approx 8\times10^{-6}$1/K and coating in all experiments was silica with CTE, about 0.5×10^{-6}1/K. Presence of a significant mismatch in CTE between the coating and substrate, results in compressive stress on the substrate surface. But, since Tg of the glass substrate is rather low (Tg$\sim$780°C) silica coating could not be heated at a higher temperature, which is needed for full densification of the silica coating. So we expected it to contribute less in the strengthening than is theoretically expected. The modulus of rupture of the glass substrates, without and with silica sol–gel coating, after the same heat treatment, were calculated using expression (1)[12] and bending strength measured data:

$$MOR = 3FL/2bh \tag{1}$$

(where: F is applied load, L is support length, b and h are sample dimensions).

Since mechanism and rates of the hydrolysis and condensation reactions of TEOS and resulting structural development in silica sol are strongly effected by the solution processing parameters, one expects that changes in the reaction conditions of the coating sol could significantly effect sol–gel coating strengthening.[8] The effect of the degree of hydrolysis on the strengthening of the glass substrate are presented in Fig. 3. The figure shows the results of MOR values for coated glass substrate, as the function of the R values. R values have significant effect on the hydrolysis rate.[1] Increasing the hydrolysis rate by increasing R, for constant pH, the degree of branching of silica chains in coating sol increases which has importance for the efficiency of the sol packing on the substrate and its

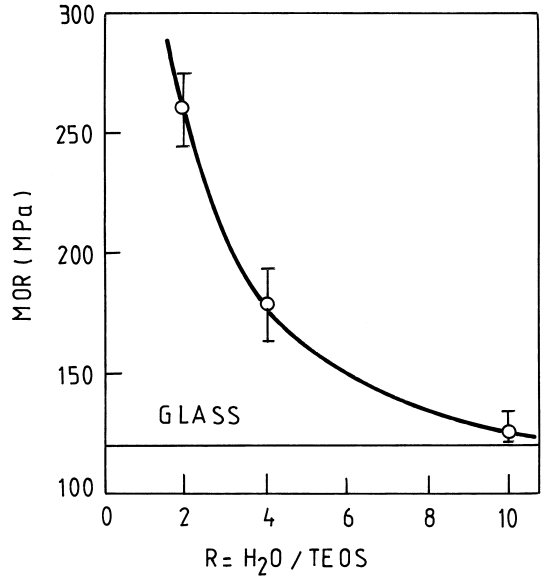

Fig. 3. MOR values for coated glass substrate as the function of the R values, (mole ratio H_2O/TEOS = R), for the samples $2C_1$, $4C_1$ and $10C_1$.

ability of bonding to the substrate.[8,14] As one can see in Fig. 3. MOR values decrease with R, but still in all cases the same degree of strengthening is obvious. The highest strengthening effect exhibits the coating $2C_1$, up to 262 MPa. This effect could be explained mainly by the coating microstructure which depends only on the chemical parameters of the coating sol. Some degree of hydrolysis is necessary to achieve strengthening, and increasing the silanol content (up to R = 2) enhances strengthening. The coating sol $2C_1$ was prepared under slow hydrolysis and condensation rate and microstructure of the $2C_1$ gel/coating consists of linear chains of silica (small degree of branching) which have a high efficiency of packing[1] (high density) and strong bonding to the substrate (since high concentration of the silanol groups). As one of the parameters which effect the substrate strengthening, one has to consider the structural inhomogeneity of the glass substrate and residual stress almost always present in the glass. But this was not the subject of this study.

Hydrolysis and condensation reactions are very sensitive to the pH value of the coating sol too.[8] The pH effect includes changes in oligomer size and free silanol content in the coating sol. Changes in sol pH values would also effect the strengthening glass substrate with silica sol–gel coating. The importance of the coating microstructure effect on the glass substrate strengthening is additionally seen on the measurement of the MOR values for the particulate sols, L_8 (MOR = 135 MPa) and $2C_8$ (MOR = 125 MPa). The oligomer size tends to decrease with increasing pH values of silica sol.[8] Besides oligomer size, changing the pH values leads to the change of silanol content. Change in the silanol content with an increase of the pH values for the silica sols L_8 and $2C_8$ could be another possible explanation for decreasing the MOR values of particulate coatings. Very small MOR values for L_8 and $2C_8$ coatings, are the result of the low ability of silica particles to bond to the substrate, since both coating sols, probably have a small silanol content. These results show the importance of the coating microstructure for the substrate strengthening.

Forming the chemical bonds between coating and glass substrate affects strengthening, and also alkaline ion diffusion (Na^+) from substrate influences the coating–substrate interaction and substrate strengthening[16] (diffusion of alkaline ion is possible at high temperature).

In Fig. 4 are given SEM microstructure of some coated glass plates after the same heat treatment at 650°C. As can be seen in Fig. 4, coating $2C_1$ has a very fine scale structure and $2C_8$ a distinctly particulate one. It was intended that this difference in the microstructure scale would be achieved in these experiments.

3.2.2 Coatings on the glass substrate with flaws

In general strengthening of glass involves penetration of the coatings into the substrate surface flaws, and chemical interaction between the coating sol and glass substrate must be important to the glass plate strengthening.

Vickers indentation was used for producing a reproducible flaw on the substrate surface before coating which could be characterised both before and after coating and breaking. The flaw was produced in order to study the possibility of strengthening the flawed glass by sol–gel silica coating, reducing C, in expression:[7]

$$Ki = \sigma_a(\pi\Omega C)^{1/2} \tag{2}$$

where Ki is stress intensity, Ω is geometric factor which depends on the shape of the flaw tip, σ_a is applied tensile stress and C is length of the surface

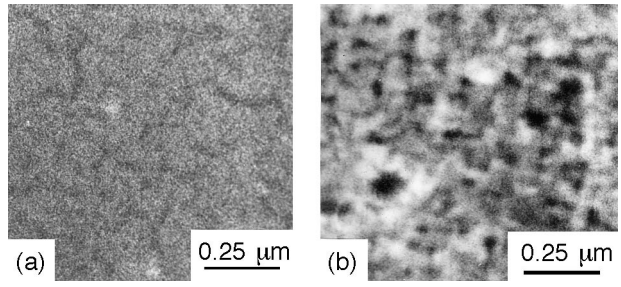

Fig. 4. SEM micrographs of the samples: (a) $2C_1$ and (b) $2C_8$.

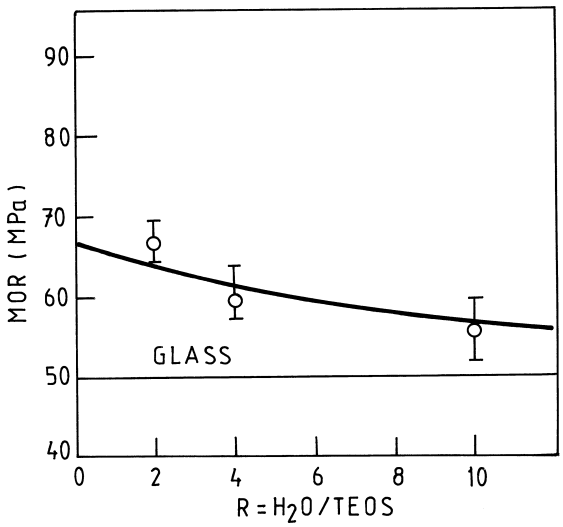

Fig. 5. MOR values of coated glass substrates, with flaws as a function of the R values (mole ratio $H_2O/TEOS = R$); for the samples $2C_1$, $4C_1$ and $10C_1$.

flaw.[8] The MOR value for indented uncoated glass substrate is 50 MPa.

In Fig. 5 are given the results of the measured MOR values of the glass substrate with coatings, as a function of the R values. As it is obvious in Figs 5 and 3 MOR values of the samples with flaws are much lower than without flaws. The next, R values, i.e. different microstructure have little influence on the strengthening of the glass substrate (MOR values being somewhat higher than uncoated glass substrate, 55.5 MPa. The reason for the very small strengthening is probably because the reduction in C is small. Small blunting crack tip is related to the relatively thin coating after heating. In order to prove this assumption, coating thickness is increased by increasing the viscosity of the coating sol (the coating thickness was estimated using data and equations from Brinker *et al.*).[17] Increasing coating thickness (Fig. 6), increases glass substrate strengthening. In contrast to the result given in Fig. 5, thicker coatings exhibit (Fig. 6) the effect of the coating microstructure on the strengthening. The highest strengthening is observed for the sample $2C_1$, which is the result of the specific microstructure, already discussed above. The lowest strengthening is again related to the particulate silica coating microstructure. Very low strengthening for particulate coating (MOR for L_8 is 53.7 MPa, the thickness less than 80 nm and for $2C_8$ is 52 MPa) is probably the result of very small penetration of particles into the flaw and small silanol content which is necessary for bonding of coating to the substrate. These results show that only the suitable microstructure and coating thickness could provide strengthening for the glass substrate.

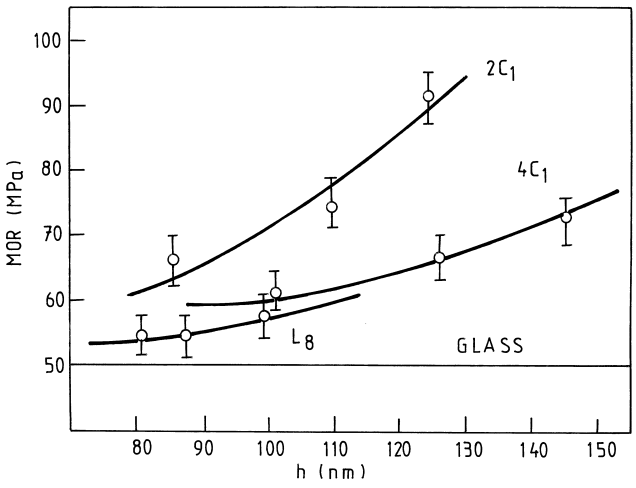

Fig. 6. MOR values of the coated glass substrates as a function of the coating thickness.

4 CONCLUSIONS

The effect of the microstructure of silica sol–gel coatings on the alkali glass substrate strengthening were investigated. The coating microstructure is related to the processing parameters of silica sol preparation. As variables in silica sol preparation, the water content (R from 2 to 10) and pH value (from 1 to 8.5) were used.

The experimental results of strengthening showed that: the highest strengthening of silica coating is exhibited by one consisting of linear chain like silica ($pH = 1$, $R = 2$). Besides, specific silica structure, the strengthening was explained with strong bonding of coating to substrate (which is the function of the number of silanol groups); the lowest degree of strengthening exhibits the particulate silica coatings ($pH = 8.5$, $R = 2$ and sol L_8). The low strengthening is explained by low coating density and the small number of silanol groups, which is characteristic of the particulate silica sols.

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