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Vickers Crack Nucleation of Glass Sheets Coated by Thin Silica Gel Layers

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SiO_2 gel layers of different thickness have been deposited on glass sheets by dipping from gelling solutions with different concentrations of silicon alkoxide. Some mechanical properties of the coated samples such as hardness (H), elastic modulus (E), crack formation tendency, and tensile stress in the film (σ) have been measured by microindentation techniques and slide deflection. SiO_2 films deposited from more dilute solutions had lower H, E, and σ values, accounting for the observed higher resistance to crack nucleation in comparison with that found for samples prepared from more concentrated solutions. [Key words: sol–gel, coatings, mechanical properties, silica, hardness.]

AMONG the various exploitations of the sol–gel method, one of the most important and popular applications remains the deposition of thin layers over glass sheets to improve their physical and chemical features.[1,2] In these cases the dip-coating method appears the most suitable for the thickness and uniform composition of the deposited layers.[3]

More recently, interest in research on this topic has been extended to the mechanical properties of the coating systems: a marked reduction in both crack propagation[4,5] and crack nucleation[6] has been found in comparison with uncoated substrates.

In an attempt to define the mechanical behavior of gel-coated sheets from the point of view of crack formation by Vickers indentation, two opposite phenomena must be considered: The low hardness and low elastic modulus of the film may decrease the intensity of the indentation stress field, whereas the presence of a permanent tensile stress in the coating may favor crack initiation. Hardness, elastic modulus, and residual stress fields are determined by processing variables such as solution concentration, the degree of hydrolysis of the precursors, and thermal treatments. In the present paper some of these aspects were taken into consideration in the case of SiO_2 gel films on soda–lime glass sheets.

EXPERIMENTAL PROCEDURE

Microscope slides of soda–lime glass were annealed at 530°C for 24 h to relieve any residual stress. They were then soaked for 1 day in doubly distilled water at 25°C to enhance the surface hydroxyl content and promote adhesion between substrate and gel coating, as reported in Ref 6. SiO_2 sol–gel coatings of different thicknesses were obtained with the dipping procedure by varying the withdrawal rate from 8 to 36 cm/min. Two solutions with different concentrations of the silicon alkoxide precursor, 50 g of SiO_2/L (SiO_2-50) and 100 g of SiO_2/L (SiO_2-100), were prepared by dissolving tetraethyl orthosilicate (TEOS) and H_2O (molar ratio H_2O/TEOS=5) in ethanol and adding HCl as catalyst.

Dipping was performed at constant temperature and partial pressure of ethanol and water, 60 to 100 min after the preparation of the solutions. During this time interval the viscosities of the solutions, 0.016 P (1.6×10^{-3} Pa·s) for SiO_2-50 and 0.050 P (5.0×10^{-3} Pa·s) for SiO_2-100, were constant. Immediately after the coating the samples were heated up to 60° or 400°C for 2 h. Double-layer samples were obtained by dipping, according to the above procedure, an already coated sheet heated at 60°C for 2 h. The so obtained specimens were thereafter processed as for the monolayer samples.

The thickness of the coatings was evaluated by a commercial profilometer, testing five samples for each treatment.

Crack formation was evaluated by a Vickers diamond pyramid hardness test. Above the threshold load, well-defined radial cracks extended from the indentation corners. The number of corners with cracks increased with loading from zero to a maximum of four. The crack-formation tendency can be expressed by the *crack propensity index* (CPI) defined as the number of developed cracks divided by 4. For individual indents this index can have values of 0, 0.25, 0.5, 0.75, or 1 depending on whether or not zero, one, two, three, or four cracks emanate from indent corners. CPI values for each load were averaged over 30 indentations. For each samples CPI values were measured for at least three different loads, allowing the drawing of crack propensity index vs indentation load curves. Vickers tests were performed in air with a constant loading time of 15 s. The number of developed radial cracks was evaluated 15 s after the withdrawal of the indenter.

Vickers hardness was evaluated together with elastic modulus measurements resulting from Knoop indentation tests[7] with a load of 0.25 N. The diagonals of the impressions for both tests were measured by using SEM facilities.

The intrinsic stress field in the film was evaluated by measuring the inflection of thin (0.15 mm thick) glass sheets coated on only one face. The intensity of the stress in the coating was determined by applying the formulation

$$\sigma=4EB^2f/3(1-\nu)L^2b$$

where E and ν are, respectively, Young's modulus and the Poisson coefficient of the substrate, B its thickness, L its length, b the film thickness, and f the measured deflection of the coated beam, considered simply supported at the ends. As the sheets were not perfectly flat, the effective inflection was evaluated by the difference of the same uncoated sheet as the average value of three different width measurements.

RESULTS AND DISCUSSION

Table I reports hardness H and elastic modulus E for some selected samples, as determined from Vickers and Knoop indentation experiments. Considering that our measurements result from mechanical properties of the gel layer and glass substrate, the lower load available was used to enhance the contribution of the thin gel film. While gel coatings generally lower both H and E values in comparison with the glass substrate, a marked difference was observed as the film deposition parameter changed. Thus, sample 3, with the same thickness as sample 1, displays considerably lower H and E values which must be directly related to intrinsic differences in the H and E values of the film only. This fact can be explained by the chemical procedure used, the consequence being that the coating obtained from the

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Table I. Experimental Thickness and H and E Values for Some Selected Samples Heated at 60°C for 2 h

Sample	Precursor solution	Thickness (μm)	H (GPa)	E (GPa)
1 (one layer)	SiO_2-100	0.38±0.03	4.8±0.8	65.0±8.8
2 (one layer)	SiO_2-50	0.18±0.02	4.3±0.4	47.0±8.0
3 (double layer)	SiO_2-50	0.38±0.03	4.2±0.3	40.0±4.0

Table II. Experimental Thickness and Tensile Stress (σ) Values for Some Selected Samples

Sample	Precursor solution	Heating temp (°C)	Thickness (μm)	σ (MPa)
1 (one layer)	SiO_2-100	60	0.38±0.03	118.8±28.4
1 (one layer)	SiO_2-100	400	0.26±0.02	181.6±36.3
2 (one layer)	SiO_2-50	60	0.18±0.02	63.0±13.9
3 (double layer)	SiO_2-50	60	0.38±0.03	60.1±9.7
4 (one layer)	SiO_2-50	60	0.40±0.03	76.0±9.9

more diluted solution displays more "plastic," i.e., less stiff, behavior than that prepared with higher concentrations of SiO_2.

Table II reports tensile stress σ values, together with the thickness of the layers for some samples studied here. Our data, obtained from strictly mechanical experiments, are in good agreement with those calculated by the indirect optical approach.[8] Samples prepared from different solutions at different concentrations display residual tensile stress fields in the silica gel layer, the intensity of which is inversely dependent on solution concentration. On the other hand, a net increase in σ was observed by increasing the temperature from 60° to 400°C. The layer thickness effect seems to play a minor role in determining σ values, in agreement with literature reports.[9] The presence of a permanent stress field in the coating is due to gel shrinkage as a consequence of solvent evaporation and density increase. The latter may be explained by physical or chemical factors such as pore elimination or Si–OH group condensation. Solvent evaporation is more favored at lower temperatures, whereas pore reduction requires more drastic firing. The intensity of the tensile stress field in the coatings depends on the degree of shrinkage and its elastic modulus; it seems reasonable that the degree of shrinkage of the SiO_2 film obtained from more diluted solution should be higher than that prepared from the more concentrated solutions, because of the higher amount of solvent that must be removed from them. Thus, the lower value of σ in the latter case must be completely explained by the lower value of its elastic modulus.

It is straightforward to explain the increased value of tensile stress in the sample heated at 400°C by shrinkage and increased stiffness of the resulting densified coating. For samples obtained from diluted solutions, the residual stress field after treatment at 400°C was not measured because of the observed detachment of the underlying film. This may be attributed to greater shrinkage, which overwhelms the chemical interaction between gel film and glass support. Indeed, enough large residual coated areas allowed the measurement of the tendency to cracking.

CPI trends for samples prepared from two different solutions with different SiO_2 concentrations and heated at 60° and 400°C are shown in Fig. 1. These trends are similar to those already described in a previous paper.[6] As a general feature the gel coating improves resistance against crack formation for low-temperature treatments; analogously, the reduced CPI of a glass sheet promoted by surface hydrolysis was attributed to the occurrence of a thin (1000 Å (100 nm)) plastic overlayer;[10] however, CPI data resulting from Vickers indentation experiments may be directly related to the surface residual stress field which is superimposed on the indentation stresses. On these grounds, the low H and E values of gel layers afford a net reduction in the intensity of the surface stress field determined by indentation. Therefore, it is reasonable that coatings obtained from diluted solutions are more effective against crack formation than those obtained from more concentrated solutions according to the H and E values of Table I. The presence of a residual stress field in the gel coating does not alter this general picture; indeed, the more plastic and deformable coatings display lower σ values.

For chemically homogeneous samples, a layer thickness increase improves resistance to crack nucleation, since the sample approaches the CPI response of bulk gels, which is 1 order of magnitude lower than that of bulk glass.[6] This fact explains the CPI improvement observed for the double-layer samples, in comparison with the thinner monolayer ones, in spite of their similar H, E, and σ values. The observed negative effect of the temperature increase is consistent with the concomitant increase of H, E, and σ in these samples.

The conclusions of the present work may be exploited for dip-coating applications of sol–gel processes in which higher concentrations of the solution are used to increase coating thickness. As concentrations are increased, the obtained coatings are chemically and physically different from those obtained by subsequent depositions from more diluted solutions. As far as mechanical properties are concerned, these experimental results indicate that coatings obtained from more concentrated solutions display higher values of hardness, elastic modulus, and residual tensile stress, affording lower improvement against crack formation in comparison with coatings from more diluted solutions.

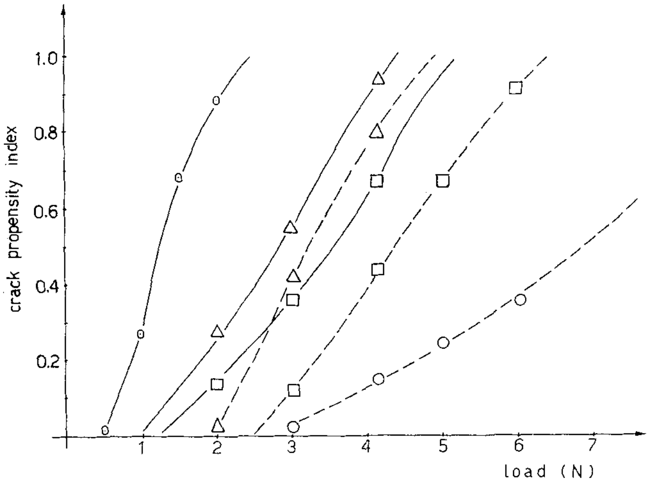

Fig. 1. Crack propensity index (CPI) vs indentation load for some selected samples: (⊙) uncoated glass; (□—□) one-layer sample obtained from SiO_2-100 precursor solution, thickness 0.48 μm, heating temperature 60°C; (△—△) one-layer sample obtained from SiO_2-100 precursor solution, thickness 0.60 μm, heating temperature 400°C; (□---□) one-layer sample obtained from SiO_2-50 precursor solution, thickness 0.25 μm, heating temperature 60°C; (△---△) one-layer sample obtained from SiO_2-50 precursor solution, thickness 0.24 μm, heating temperature 400°C; (○---○) double-layer sample obtained from SiO_2-50 precursor solution, thickness 0.60 μm, heating temperature 60°C.

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