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Indentation properties of ZrO_2–SiO_2 coatings on glass substrates

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Abstract

Sol–gel coatings of different composition in the ZrO_2–SiO_2 system have been prepared, starting from several precursors (alkoxides and alkylalkoxides). Common soda lime silicate glass slides were used as substrates for coating deposition. The Vickers microhardness,H_V, of the coated glass substrates have slightly higher values than that of uncoated glass. Young modulus, E, values for coated glass substrates are higher than that of uncoated glass. To compare the mechanical properties of the samples, the ratio H_V/K_{IC} (where K_{IC} is the toughness) has been calculated and the concept of fragility discussed. The fragility of coated samples increases as the ZrO_2 content diminishes and the SiO_2 increases. Both scanning and transmission electron microscopy observations were performed to characterise the textural and microstructural properties of the coatings.

Keywords

A. ZrO_2–SiO_2 system; C. Sol–gel coatings; D. Indentation property

1. Introduction

The application of coatings that modify the properties of glassy substrates is an effective method for obtaining materials with better or new performances. Sol–gel glassy coatings have been previously applied upon different substrates providing good adherence on ceramic materials, metals, polymers, glasses, alloys, etc. [1], [2], [3] and [4]. Moreover, good thermal, chemical, mechanical, and optical properties can be achieved. They are also suitable for corrosion protection [5] and confer interesting optical properties to the material surface giving rise to reflecting [6], non-linear [7], coloured [8], luminescent, thermochromic[9], photochromic [10] and electrochromic [11] effects (among others). As far as mechanical properties are concerned, sol–gel coatings are resistant to scratching, peeling and delamination, protecting the substrate from stresses [12], [13], [14] and [15]. The protection mechanism that is usually regarded as responsible for such behaviour involves the curing of the substrate surface by the thin film. The coating is applied at room temperature as a liquid (sol) that fills small pits

and microcracks on the substrate, forming a new homogeneous surface resistant to crack propagation.

Pure silica coatings have been generally prepared by the sol–gel method studying their main properties (mechanical ones included). Zirconia containing thin coatings obtained by sol–gel have been prepared and characterised [16], [17] and [18]. Nevertheless, some aspects related to their mechanical properties are still unexplored. Therefore, the aim of this paper is to report and discuss the role of silica and/or zirconia sol–gel coatings on the mechanical properties of conventional glass substrates, by means of indentation measurements. The final objective is to use these coatings as matrices for encapsulating organic dyes suitable for production of optical sensors, for which parameters that have to be taken into account, include, soft densification temperature and presence of residual organics from precursors.

2. Experimental

Different compositions in the ZrO_2, ZrO_2–SiO_2 and SiO_2 systems were prepared to obtain sols (Table 1), starting from tetraethoxysilane ($Si(OEt)_4$), dimethyldiethoxysilane ($Si(Me)_2(OEt)_2$), zirconium tetrabutoxide ($Zr(OBu)_4$) together with deionised water, hydrochloric acid, ethanol and some additives to adjust the rheological properties of the sol, as described elsewhere [18].

Table 1. Sample composition and precursors used

Sample no.	Composition (mol%)		Precursors (mol%)[a]	
	ZrO_2	SiO_2	ZrO_2	SiO_2
1	100	–	ZTB[b] (100)	–
2	50	50	ZTB (50)	TEOS[c] (50)
3	50	50	ZTB (50)	M2E2S[d] (50)
4	–	100	–	TEOS (100)
5	–	100	–	TEOS (50), M_2E_2S (50)

[a] Numbers in parenthesis indicate molar percentage.

[b] ZTB: zirconium tetrabutoxide.

[c] TEOS: silicon tetraethoxide.

[d] M_2E_2S: dimethyldiethoxysilane.

Samples 3 and 5 (hybrid samples) were prepared from a mixture of an alkoxide and an alkylalkoxide. The alkylalkoxide used (dimethyldiethoxysilane, M_2E_2S) has two groups that can be hydrolysed (two ethoxy groups) during the sol preparation; and other two groups that cannot be hydrolysed (two methyl groups). Since only two positions will be hydrolysed per molecule, only such positions would be sites for later polycondensation; while the two methyl groups will

remain non-hydrolysed and non-polycondensed. This is the reason why the resulting material will be mentioned as organic–inorganic hybrid in the following results and discussion chapters. The organic part corresponds to the methyl groups. The organic part corresponds to the methyl groups. The precursor of the inorganic part corresponds to the ethoxy groups ($–OC_2H_5$) that were hydrolysed to –OH groups, which then polymerise forming siloxane bonds (Si–O–Si) and/or Zr–O–Si and Zr–O–Zr bonds after densification.

Samples 2 and 4 (non-hybrid samples) were prepared from an alkoxide. All the four groups of alkoxides used can be hydrolysed and then polycondensed. After densification, the network is formed by Si–O–Si bonds and/or Zr–O–Si and Zr–O–Zr bonds, as well as residual –OH groups. This is the reason why the material is considered in the following results and discussion chapters as inorganic and, therefore, non-hybrid.

The final concentration of silicon and zirconium oxides in the sol was 120 g l^{-1} of sol. The substrates used to obtain thin coatings were chemically cleaned soda lime silicate glass slides. Application of coatings was performed by dipping the substrates into the sols and withdrawing them at a slow constant rate ranging 0.8–4.2 mm s^{-1}. Partial densification of coatings was carried out at 60 °C during 72 h. Thickness of heat-treated coatings was in the range 150–400 nm as determined by a Taylor–Hobson profilometer.

Mechanical properties of the assemblage formed by both the substrate and coating were measured with a Matsuzawa microindenter. The results (measurements carried out with a conventional microindenter) are interesting because they give information on the behaviour of the substrate+coating assemblage. In fact, the coatings prepared are usually used when applied upon a substrate, rather than isolated. Different loads were tested ranging from 10 to 1000 g. For loads lower than 500 g no mechanical parameter could be calculated, since no imprint from the indenter was obtained. Mechanical parameters from indentation tests were determined from the experiments performed with 500 and 1000 g loads, by using the expressions given in [19], following the procedure explained by Rincón and Capel [20]. Experimental errors for Vickers microhardness (H_V), Young modulus (E) and critical stress intensity factor (K_{IC}) measurements was ±0.5 GPa, ±5 GPa and ±0.1 MPa $m^{1/2}$, respectively.

Surface microstructure of coatings was observed by scanning electron microscopy (SEM) using a Philips XL30 equipment (20 kV). In addition, the porous texture of the coatings was examined by transmission electron microscopy (TEM). Simple carbon replicas of the external coating surface were prepared from fresh surfaces previously exposed to diluted HF vapour for 10 s. TEM observations were undertaken using a Hitachi 7100 microscope (125 kV).

3. Results

Table 2 shows results obtained after indentation tests performed with a 1000 g load for 15 s. Likewise, the results from indentation tests carried out with a 500 g load for 10 s are shown inTable 3.

Table 2. Average values of the mechanical parameters determined from indentation tests on sol–gel coatings on glass substrates (1000 g load, 15 s)

System	Sample no.	H_V (GPa) ($\pm\sigma = 0.05$)	E (GPa) ($\pm\sigma = 10$)	K_{IC} (MPa $m^{1/2}$) ($\pm\sigma = 0.05$)	$B = H_V/K_{IC}$ ($\pm\sigma = 0.05$)
ZrO_2	1	5.0	220	1.6	3.25
ZrO_2–SiO_2	2	4.9	85	1.5	3.30
	3	5.2	69	1.4	3.71
SiO_2	4	4.8	70	1.1	4.36
	5	5.0	62	0.9	5.56

Table 3. Average values of the mechanical parameters determined from indentation tests on sol–gel coatings over glass substrates (500 g load, 10 s)

System	Sample no.	H_V (GPa) ($\pm\sigma = 0.05$)	E (GPa) ($\pm\sigma = 10$)	K_{IC} (MPa $m^{1/2}$) ($\pm\sigma = 0.05$)	$B = H_V/K_{IC}$ ($\pm\sigma = 0.05$)
ZrO_2	1	5.1	47	1.8	2.88
ZrO_2–SiO_2	2	5.3	61	2.8	1.92
	3	5.5	88	3.0	1.85
SiO_2	4	6.0	97	1.2	5.17
	5	5.8	72	2.8	2.06

Each value in Table 2 and Table 3 corresponds to an average calculated from at least 10 indentations performed on each sample from, at least, four series of samples of different thickness, ranging from 150 to 400 nm. Vickers indentations with loads of 500 and 1000 g upon coatings of 150–400 nm thickness have deeper penetration than the coating thicknesses. Thus, the mechanical parameters determined correspond to the response of the coated glass substrate. If the parameters measured on the substrate+coating assemblage were exclusively the response of the substrate, we should obtain the expected values for common soda lime silicate glass. However, we obtained different values that we attribute to the surface modification of the substrate by the coatings, as discussed below. No relationship between coating thickness and the different mechanical parameters was found. This indicates that mechanical behaviour of the substrate+coating is independent of the coating thickness, at least when such a thickness is in the order of a few hundred nanometres. On the other hand, the average values calculated allow comparison of the samples according to their characteristics.

Thus, even though the loads used were higher than nanoscopic indentation method and the results are from the assemblage: glass+substrate, three main factors should be kept in mind in order to discuss data from Table 2 and Table 3. These are the following:

1. load with which the indentations were performed;
2. composition of coatings, i.e. the percentages of ZrO_2 and SiO_2; and
3. whether the precursors used were alkoxides (non-hybrid samples 2 and 4) or a mixture of alkoxides and alkylalkoxides (hybrid samples 3 and 5), as was explained in the former experimental chapter.

The most important feature of hybrid sol–gel materials is that they present a softer and more textured microstructure than non-hybrid materials. Porosity, when present, shows wider pore size distribution and pore diameters than non-hybrid materials. In the case of hybrid sol–gel coatings, thicker layers can be obtained in comparison with the non-hybrid coating counterparts.

For Vickers microhardness (H_V), a small increase was observed for samples with pure silica coatings when tested under a 500 g load. Hybrid samples (3 and 5) seem to show some higher H_V values compared with non-hybrid and/or inorganic samples (2 and 4, respectively). This especially occurs for zirconia coatings (compare samples 2 and 3), while the silica coatings samples do not present any remarkable tendency (compare samples 4 and 5). H_V values obtained from indentation tests with a 1000 g load are about 5 GPa, while the values obtained with 500 g load are between 5 and 6 GPa. These results can be explained on the basis that with low load the indentation penetration is smaller than with 1000 g, and the response of the material contains a higher contribution from the coating. However, for a 1000 g load, the material response can be considered as the modified behaviour of the glass substrate influenced, to some extent, by the sol–gel coating. It seems, therefore, that the coating acts as a softening layer, which attenuate the indentation effect. The results also indicate that coating microhardness is higher than that found for monolithic sol–gel materials with the same or even more densification degree, which is in agreement with previous research performed on sol–gel borosilicate glassy materials [21]. In addition, Vickers microhardness of common soda lime silicate glass coated by the sol–gel films prepared and studied in the present paper, shows values (average 5.0 GPa) slightly higher than that of uncoated common glasses 4.5–5.0 GPa [22], probably due to the elastic effect of the sol–gel coating.

The Youngs modulus clearly increases with ZrO_2 content when a 1000 g load was used (up to 220 GPa), while the samples with pure silica coatings have higher E value for a 500 g load. Nevertheless, under a 500 g load all the samples have Youngs moduli of the same order of magnitude, varying from 47 to 97 GPa. Regarding the influence of the hybrid precursor, the data collected in Table 2 (1000 g load) show a decrease from 85 to 69 GPa in samples 2 and 3, respectively; and from 70 to 62 in samples 4 and 5, respectively. However, in Table 3 (500 g load) a clear trend cannot be seen. Despite the dispersion in the results, the E values for coated glass samples are higher than the Youngs modulus of uncoated glass (55–65 GPa) [22].

Critical stress intensity factor, K_{IC} (toughness), increases slightly with ZrO_2 content under 1000 g load (Table 2, sample sequence: 4, 2, 1, whose K_{IC} is 1.1, 1.5 and 1.6 MPa $m^{1/2}$, respectively). A remarkable influence of hybrid samples can be accounted for samples with pure silica coatings when a 500 g load was used, i.e. an increase from 1.2 (sample 4) to 2.8 (sample 5) (Table 3). Similarly to the values obtained for Vickers microhardness, K_{IC} shows higher values for the series tested under 500 g load (average, 2.29 MPa $m^{1/2}$), while the series tested under 1000 g load present values (average, 1.29 MPa $m^{1/2}$) closer to that of uncoated soda lime silicate glass (0.8–0.9 MPa $m^{1/2}$) [22]. This indicates that both silica and zirconia coated substrates have higher fracture resistance than uncoated conventional soda lime silicate glass.

Finally, the calculated ratio H_V/K_{IC} can be discussed in terms of sample fragility (B) [23], or as a parameter directly related to the superficial fragility of the substrate coated by the sol–gel film. A correlation between the composition and B seems to be clear in the results obtained with a 1000 g load (Table 2): the fragility increases as the ZrO_2 content diminishes or the SiO_2 increases. Thus, the samples with silica coatings behave as the most superficially brittle. In Table 3, the B data are influenced by the respective values of H_V and K_{IC}, which could account for the disperse results. Too high B values (e.g. sample 4 in Table 3) could be due to the presence of defects on the coating surface, such as microcracks or delamination which could contribute strongly to a decrease in the corresponding K_{IC} value.

SEM observations displayed the surface texture of the coatings prepared. Fig. 1a–c shows micrographs of samples 3–5, respectively. A very fine and homogeneous surface microstructure is observed together with small cracks (Fig. 1a and c), that have been occasionally developed during the partial densification treatment. The formation of such cracks could account for the dispersion found in the mechanical parameters measured, as mentioned above. A global analysis of the SEM images from all the samples prepared, confirmed that the higher the ZrO_2 content, the more likely the tendency to develop microcracks during densification, even though the superficial texture be different aspect.

In regard to the effect of hybrid precursor on the microstructure of coatings, the only noticeable feature is a more grain shaped texture, as can be seen in Fig. 1c. Nevertheless, a direct correlation between that feature and the results obtained for mechanical parameters was not apparent.

Fig. 2 shows a transmission electron micrograph (TEM) of sample 5, which reveals the homogeneous porous inner texture of the coating and the absence of crystalline nuclei or incipient devitrification. In fact, the sponge-like microstructure could be responsible for the observed improvement in the mechanical properties, since such texture could delay propagation of stresses and fracture cracks. In some samples, detection of crack propagation during indentation tests was not possible.

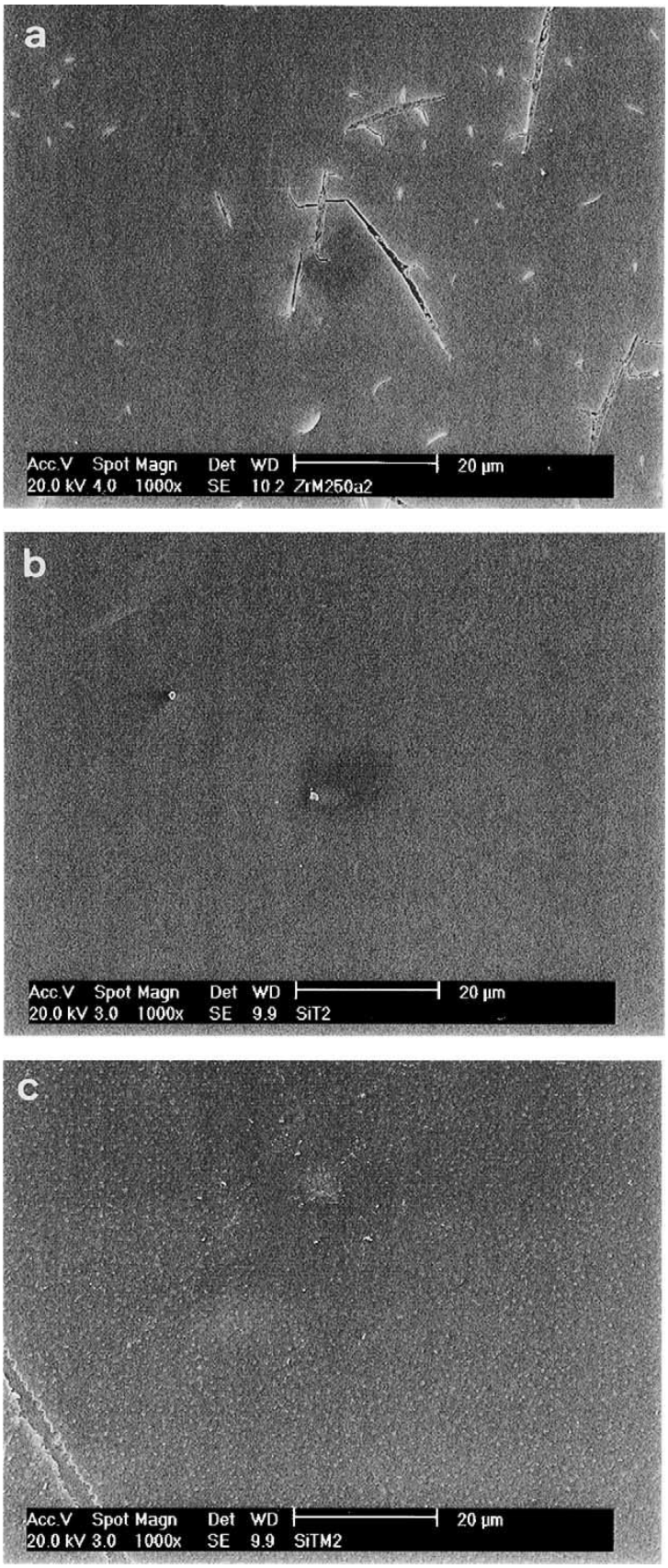

Fig. 1. SEM micrographs from the surface of coatings in (a) sample 3, (b) sample 4 and (c) sample 5.

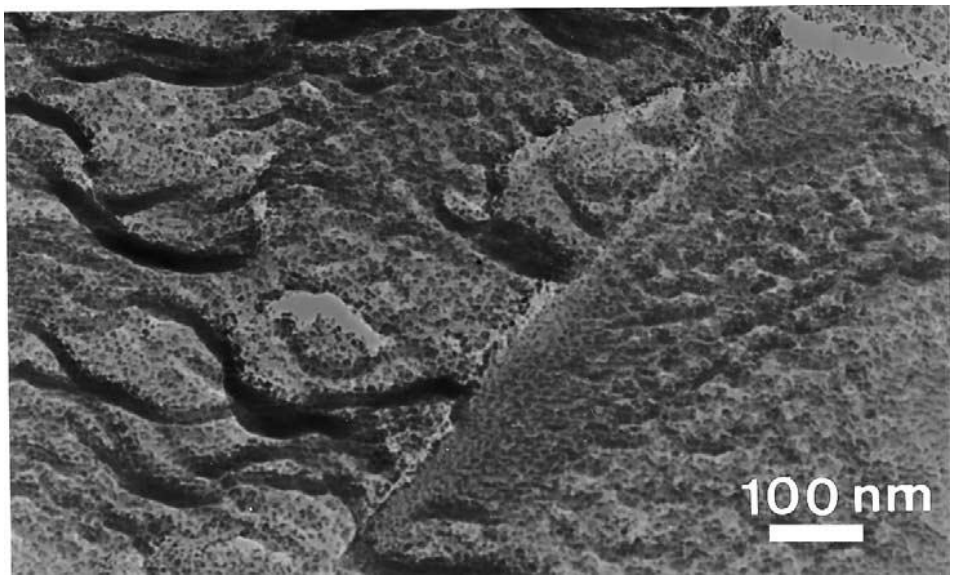

Fig. 2. TEM micrograph of sample 5 obtained from a simple carbon replica of the coating surface etched with diluted HF vapour.

4. Discussion

Comparison of indentation results from Table 2 and Table 3 could give information on the differences in mechanical properties of the hypothetical free-standing sol–gel film and the behaviour of the material formed, a combination of the common glass substrate and the thin coating, i.e. how the sol–gel coating can affect the mechanical properties of the glass substrate surface. Obviously, our knowledge about the mechanical properties of the isolated coatings is indirect, due to the difficulty of handling them without a substrate. Thus, the only attainable information comes from the measurements performed on the substrate+coating assemblage and the sol–gel monolithic material densified at the same temperature. In the latter case, the behaviour of both monolith and coating of the same composition is likely to be quite different. Since drying, densification, shrinkage and residual porosity are likely to be different. Moreover, partially densified coatings at a given temperature (in this case up to 60 °C) reach a higher densification degree than monoliths of the same composition, for the same treatment. This is due to the very different drying process which depends, among other parameters, on the distance (thickness, if coatings) that solvents and water must cross to reach the free surface in order to be released. Thus, mechanical properties of the corresponding sol–gel monoliths should not be compared directly with those of the coatings. This is one reason why mechanical properties of sol–gel coatings have been explored indirectly by studying the behaviour of the substrate-coating assemblage. Apart from nanoindentation techniques, indentation experiments can be a proper approach to study the mechanical response of the coated glass as a system formed by two

materials (substrate and coating) that closely influence each other due to their common glassy nature.

With the aim to summarise the influence of both the silica and zirconia proportion and the kind of precursor used for coating preparation, we consider two groups of measurements. As mentioned above, those obtained for 500 g load are more related to the coating role in the assemblage (substrate+coating); while those obtained for 1000 g load closely refer to the substrate response modified, to some extent, by the coating.

Thus, for measurements performed with 500 g load, the higher is the zirconia content, the lower are the H_V, E and B values and the higher are the K_{IC} values. Obviously, the silica content induce the inverse tendency. This means that coatings with zirconia are the most elastic and tough and the least fragile and hard. The presence of zirconium ions in two different coordination environments (as glass-forming ions with coordination number 4, and as glass-modifying ions with coordination number 6), probably determines a mixed glassy network with the former properties.

The use of the hybrid precursor affects the mechanical properties in this sense: independently of the composition, toughness increases and fragility decreases; and the simultaneous presence of zirconia and the hybrid precursor enhances H_V and diminishes E. In other words, the sample behave as a more resistant and elastic material. This is probably a consequence of the residual organic groups from the organic–inorganic precursors and/or of the microporosity generated after densification, by thermal release of those organic groups.

On the other hand, the results obtained for 1000 g load indicated that the proportion of silica and zirconia has negligible effect on the microhardness; while E and K_{IC} values increase and B values decrease with the zirconia content. That is, the coating influence in the mechanical response of the substrate is in the sense of a more tough, rigid and less fragile material. Conversely, the use of a hybrid precursor does not seem to affect the tendency observed when such precursor is not used. Thus, what modifies the substrate behaviour is the fact of being coated by a sol–gel layer rather than the particular composition or the kind of precursor used. Nevertheless, a positive influence of zirconia cannot be discarded, since, as already noted, zirconia determines a more tough, rigid and less fragile material.

Results obtained demonstrated the mechanical role of the sol–gel coatings and their protective character. Whether such protective effect is due to the curing of the glass substrate microcracks at the surface or is a result of the direct mechanical response by the sol–gel coating, is still under discussion and a subject of current research. However, the microporous texture of sol–gel coatings together with their high homogeneity seem to be factors working in the same sense, favouring improvement of the mechanical properties.

Experimental fragility values determined in the present work allow also their classification into either the same group of conventional glass ceramic tiles (tests performed with a 1000 g load, reflecting mechanical behaviour of the common glass substrate modified by the coating) or the

group of porcelain stoneware tiles (tests performed with a 500 g load, reflecting an approach to the mechanical behaviour of the sol–gel coating itself)[23] and [24]. In both cases, the mechanical response of the conventional glass substrate has been improved to the values of materials currently used to resist scratches, impacts and abrasion.

Since the sol–gel coatings studied here were designed and prepared to encapsulate organic dyes for sensing purposes, no aggressive mechanical treatment is expected to be performed upon their surface, except for soft scratching due to handling in the sensing device. Bearing in mind the present results, common glass coated by these sol–gel thin films could be used as a mechanically adequate material.

5. Conclusions

Thin sol–gel coatings in the systems ZrO_2, SiO_2 and ZrO_2–SiO_2 have been prepared upon common soda lime silicate glass, starting from different precursors (alkoxides and a hybrid alkylalkoxide). Mechanical behaviour of the partially densified samples has been studied by means of indentation tests, mainly performed under 500 and 1000 g loads. Parameters such as Vickers microhardness (H_V), Young modulus (E), critical stress intensity factor (K_{IC}, toughness) and fragility (H_V/K_{IC}) were determined.

Coating thickness does not affect the mechanical properties measured, at least in the range 150–400 nm. Increased H_V values were obtained for samples with $50ZrO_2{\cdot}50SiO_2$ coatings, especially when the hybrid precursor is used as a silica source. In general, the sample (substrate+coating) fragility is higher for those prepared with the hybrid precursor (1000 g load tests). Substitution of ZrO_2 by SiO_2 increases the coating microhardness and fragility. The occasional presence of microcracks in the coatings surface, generated during the thermal densification, could affect the fragility values as well as the behaviour of samples with different proportion of ZrO_2 and SiO_2.

In samples with pure silica coatings (1000 g load tests), the substitution of the non-hybrid precursor by the hybrid one increases both microhardness and fragility values. Samples with pure silica coatings are the more brittle than those coated by ZrO_2 and ZrO_2–SiO_2 sol–gel films. Electron microscopy observations allowed the correlation of the surface microstructure and the inner homogeneous porous texture of coatings with the mechanical behaviour of the sample formed by the glass substrate and the sol–gel coating.

The sol–gel coatings investigated are quite mechanically adequate for their final application as solid state hosts for organic dyes in sensing applications, when applied to common soda lime silicate glass substrates.

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