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OPTICAL AND MECHANICAL CHARACTERIZATION OF ZIRCONIUM BASED SOL-GEL COATINGS ON GLASS

The basic factor limiting the use of glasses is their unsatisfactory mechanical strength. The improvement of the mechanical strength of glasses is usually obtained by applying their respective thin surface layers. The object of the research was glass coated with zirconium oxide. For the application of zirconium oxide layer, dip-coating method was used. The resulting materials were subjected to detailed examination of the microstructure (SEM), and mechanical tests (Vickers hardness and modulus of elasticity). In order to evaluate the optical characteristics, the tests were performed by UV/VIS. The thickness of the overlying layers were determined using the method of ellipsometry. The study showed that the obtained sol-gel layer of zirconium oxide (IV) on glasses influence the improvement of the mechanical properties. It has been shown that the applied layers have high adhesion to the substrate.

Keyword: sol-gel coating, zirconium oxide, ellipsometry, Vickers hardness

1. Introduction

The theoretical strength of glasses in the literature is about 7000 [MPa] and relates to a defect-free glasses (pristine glass). The introduction of defects results in a rapid decrease of strength and practical strengths are about 1% of the theoretical value (35-70 [MPa]). It can be assumed that the presence of surface defects significantly reduces the strength of glasses. Most often surface defects are located in the glass layer having a thickness of 1-10 [μm] [1,2]. The strength of glasses is conditioned by the state of its surface and can be estimated with the Griffith equation. There are several ways to increase the mechanical strength of glasses [3]. According to Bartholomew'a [4] glasses strength can be improved at the stage of their manufacture or by modified the surface of finished product. Flame polishing and chemical etching glasses are effective methods that allow only a temporary increase strength of the glasses. A more effective way is laser cutting edge of the glasses [4] or chemical strengthening of the glasses by an ion exchange process combined with flame treatment (ie. the method mixed).

A number of methods have been devised for generating surface compressive stresses in line with Bartholomew's second approach [4]. Among these methods the improvement of the glass strength can be achieved by thermal strengthening, ion-exchange, vitreous enamelling or by cladding with a material of lower thermal expansion coefficient [5]. According to Varshneya effective protection of the surface layer of the glasses provides a compressive stress layer having a thickness of about 30[μm] [6]. Different approach of glass surface refining was proposed by Drajewicz. Aluminum compounds of nano-powders were spread onto the heated glass surface [7]. Another way to improve the strength of the glasses is to apply on their surface the protective coating obtained by the chemical reaction during the formation of these coating. Typical coatings on a glass are sol-gel coating made on the basis of organosilanes and coating hybrid organic-inorganic which have been resulted from the chemical reaction [8]. The increase in the mechanical properties of glasses can be achieved by the coating of zirconium oxide (ZrO_2) [9]. The tetragonal polymorph of zirconium oxide is characterized by the high values of hardness and Young's modulus. In addition the ZrO_2 is resistant to abrasion [10,11]. Therefore, ZrO_2 is used in many fields [e.g. 12-17]. There are many methods that allow to obtained a layer of zirconium oxide on the surface of the glasses. One of them is a method called sol-gel. This method (sol-gel) allows to obtain a thin film at room temperature [18]. The term sol-gel is commonly used to describe two processes, one starting from a colloidal inorganic sol and another using organic metal alkoxide precursors, usually in a solution with alcohol and water. The sol-gel process includes chemical reactions between colloidal particles in a sol or between polymeric species in a solution to form a gelatinous network which is then dried and sintered to a dense amorphous solid. The most commonly used coating techniques are dip- and spin-coating requiring symmetrical substrates. Generally the sol-gel process enables the preparation of oxide layers with a large variety of chemical compositions. Coatings obtained from more concentrated solutions display higher values of hardness, elastic modulus and residual tensile stress, giving less improvement against crack formation when compared to coatings produced from more dilute solutions. There is

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always a strengthening effect due to filling of surface flaws but depending on the sol-gel and the glass composition other mechanisms might also contribute [19-22].

The main aim of this study was to obtain sealed, homogeneous layers of ZrO_2 on the surface of silica-soda-lime glasses and to determine their mechanical and optical parameters. The resulting layers are intended as reinforcement and the surface-protection toughened glasses and glasses of ion-exchanged.

2. Experimental methods

The surface of silica-soda-lime glasses were degreased with ethanol. Then prepared sample surface was covered with a layer of the sol: 15 samples were coated with 2% ZrO_2 sol, and another15 samples were coated with 4,9% ZrO_2 sol. The following precursors were used: acetic acid 80%-$C_2H_4O_2$ 60,05[g/mol], the company CHEMPUR (zirconia sol 2%), acetic acid 99,8%-$C_2H_4O_2$ 60,05 [g/mol], the company CHEMPUR (zirconia sol 4,9%), ethyl alcohol 99,8%-C_2H_5OH, POCH-Polish Chemical Reagents, propoxide, zirconium (IV) 70%-$Zr(OC_3H_7)_4$, ALDRICH, nitric acid approx. 65%-HNO_3, POCH-Polish Chemical Reagents. The preparation of sols was started with the preparation of laboratory equipment. Magnetic Stirrer model MS 11 HS was connected to the network and started setting the rotational frequency of approx. 500 rev/min. The Erlenmeyer flask was placed on a magnetic stirrer. The amount of ethyl alcohol (C_2H_5OH) was measured using a graduated cylinder. A small part of alcohol was putted into Erlenmeyer flask placed on vibrating magnetic stirrer. Acetic acid (CH_3COOH) and an appropriate amount of nitric acid HNO_3(V) (for zirconium sol 4,9%) was added. Another precursor added to the stirred solution was propoxy derivative of $Zr(OC_4H_9)_4$. Finally residual ethanol was added (portion wise). The last portion of alcohol was mixed with sufficient distilled water and added to a stirred solution using a disposable pipette (drop by drop). The resulting solution was left running for 2 h. Then Erlenmeyer with a solution was stoppered and left in a refrigerator at about 5°C. In each of the groups of 15 samples the sequence of coating was as follows: 1 layer of sol + burning, 2 layers of sol + burning, 3 layers of sol + burning, 1 layer of sol +burning + 2 layers of sol +burning, 1 layer of sol + burning + 2 layers of sol + burning+ 3 layers of sol+ burning (Table 1).

TABLE 1

Methods for coating glass samples

Series	2% ZrO_2 sol	4,9% ZrO_2 sol
1	1 x sg + burn	1 x sg + burn
2	2 x sg + burn	2 x sg + burn
3	3 x sg burn	3 x sg + burn
4	1 x sg + burn 2 x sg + burn	1 x sg + burn 2 x sg + burn
5	1 x sg + burn 2 x sg + burn 3 x sg + burn	1 x sg + burn 2 x sg + burn 3 x sg + burn

An UV/VIS Perkin Elmer with integrating sphere was used to measure transmittance from 300 to 1000 [nm]. The morphologies of glass surface were examined by SEM/EDAX method with use of the scanning electron microscope SEM NOVA NANO 200. The Nano-Indentation Tester has been used to provide surface mechanical characterization data hardness and Young's modulus by indenting to depths at the nanometer-micron scales [23-25]. The CSM Instruments Micro Scratch Tester (Neuchatel, Switzerland), with a capacity up to 30 [N], were used with a 200-[μm] Rockwell diamond indenter. The scratch tests were performed with the Prescan procedure, which consists of two stages: first, the surface is scanned by the tip of the indenter with minimal load (0.03 [N]). Second, the scratch test is made, during which the penetration depth is recorded. The ellipsometric data were collected with a M-2000 Woollam ellipsometer in the spectral range 190 – 1700 [nm]. All the measurements were performed at room temperature.

The ellipsometric angles Ψ and Δ fulfill the fundamental equation of ellipsometry, namely $\tan\Psi = |r_p|^2 / |r_s|^2 \exp(i\Delta)$, where r_p and r_s are complex Fresnel reflection coefficients for '*p*' and '*s*' polarizations, respectively, and Δ is a phase shift between both polarized waves. The samples have been measured for three angles of incidence, namely 60°, 65° and 70°. To analyze the data, we have combined all the angular spectra and we have fitted all the data simultaneously [26,27]. The data have been analyzed using CompleteEASE 4.1 software.

The ellipsometric data, gathered as a function of wavelength *λ*, have been fitted in the range of low absorption, i.e. 350 – 1700 [nm]. In the region of weak absorption (above 350 [nm]), the Cauchy model for the system layer – glass, of the refractive index dispersion was applied, being expressed by formula:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \qquad (1)$$

where A,B and C are fitting parameters.

3. Results and discussion

In order to determine the surface state and chemical composition of the layers studies were performed using a scanning electron microscope (SEM) with a microanalyzer (EDAX) - Fig.1. Analysis of the chemical composition (EDAX) clearly indicated the presence of zirconium in the structure of the surface. Scanning Electron Microscopy (SEM) pictures of the films showed that the surfaces are mostly homogeneous with defects only occurring above the critical film thickness. These defects are mainly superficial and/or deeper cracks, partial delamination of the coating also occurred (Fig. 1). Energy Dispersive X-Ray Analysis (EDXA) was carried out to identify the elemental composition of a zirconium layer on a glass sample.

The study of mechanical properties of ZrO_2 coatings involved 10 samples. Each sample of glasses was coated with the sol in a different sequence. Only the best results of samples harness are shown in Figure 2. The test of the mechanical properties showed that the glasses samples coated

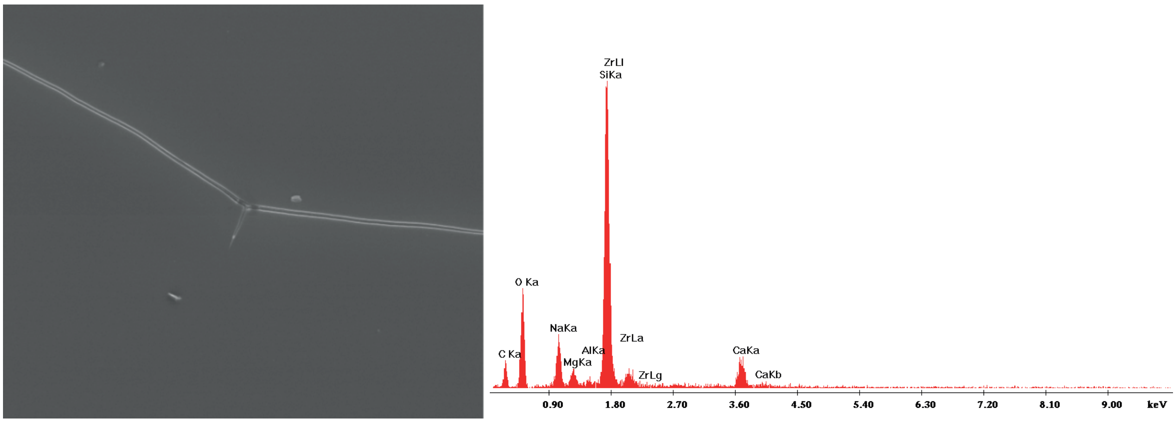

Fig. 1. SEM image of the zirconium layer and EDX analysis of the chemical composition

Fig. 2 The mechanical properties of the base glass samples and ZrO_2 coated samples: hardness HV, modulus of elasticity

with zirconium oxide have a higher value of the hardness and elastic modulus compared to the base glass - without zirconia layer (Fig.2).

The best mechanical properties of coating were observed for the following samples: PR06 - a sample of glass covered with a double layer of zirconium sol 2% and burned, PR21 - a sample of glass covered with a double layer of zirconium sol 4.9% and burned, PR30 - sample of a single layer of glass coated with zirconium sol 4.9% and burned, then covered with a double layer of zirconium sol 4.9% and burned and covered with a triple layer of zirconium sol 4.9% and burned. Based on the Vickers hardness test it can be concluded that the greatest microhardness is observed for the samples PR06 and PR30. Coincidentally these samples are characterized by the extreme thickness values. Therefore, it can be suggested, that not only the continuity of the coating but also the coating process is of a great importance and may affect the mechanical properties

Functional behavior of a coating is critical to its adhesion to the substrate. Scratch test was used to obtain the critical loads that are related to adhesion properties of coatings. Scratch Adhesion Test was performed by applying a progressive linearly increasing load.

A diamond indenter was moved over a specimen surface with a linearly increasing load until failure occurs at critical loads Lc. The scratch tests were repeated for three times in order to obtain reliable results. Lc is a function of coating substrate adhesion, stylus-tip radius, loading rate, mechanical properties of substrate and coating, coating thickness, internal stress in coating flaw size distribution at substrate -coating interface, and friction between stylus-tip and coating. The results of the maximum load and penetration depth at which the separation of a layer from the substrate occurs are presented in the table 2.

TABLE 2

The results of the scratch test

Number of samples	The critical load Lc [N]	The maximum depth of penetration of Gp [mm]
Base glass	1,76	0,53
PR06	4,54	1,20
PR21	5,92	1,65
PR30	2,72	0,60

It is noteworthy that all the coated samples resulted more scratch resistant with respect to the uncoated glass substrate. The results shown in the Table 2 indicate that the sample PR21 is characterized by the best adhesion layers to the glass substrate surface. In order to detach the coating from the substrate the greatest strength is needed (about 5.92 [N]) and diamond indenter should “stick to” the layer to a depth of 1.65 [mm] (Tab.2). Some considerations can be drawn: considering statistic error, sample PR30 and the base glass shows almost the same scratch depth.

The optical properties of ZrO_2 thin films are highly influenced by the chemical formulation, fabrication method and processing parameters. The highest transmission in comparison to the transmission of the base glass is observed for the glass sample PR06 covered with a double layer of zirconium 2% and burned (Figure 3). A significant decrease (approx. 5%) of the transmittance was recorded for a sample PR30. This sample is characterized by the greatest thickness. For the sample PR21 a decrease in transmission was observed in the range of 400-600 [nm]. In the range of 355-400 [nm], the transmittance of this sample was the same as the base glass. For all the samples the absorption edge is near to 354 [nm].

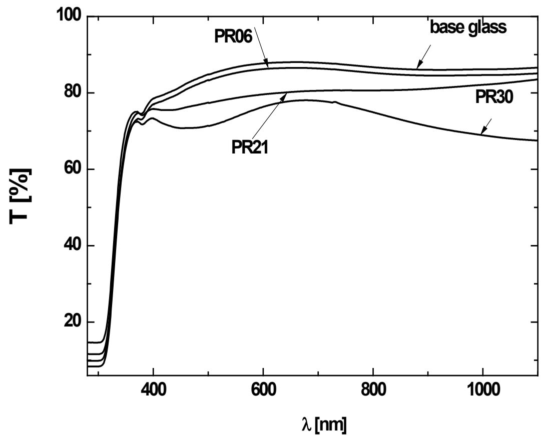

Fig. 3. Transmittance of glass samples coated with ZrO_2

The thickness and the refractive index n of the sol–gel derived ZrO_2 coatings have been determined by ellipsometric method [28]. Values of the refractive coefficient at 633 [nm], the Cauchy parameters A,B and C along with the thickness determined from the fitting procedure are presented in Table 3

TABLE 3

Refraction index at 633 [nm], Cauchy parameters and thickness obtained from ellipsometric studies

Glass	*n* at 633 [nm]	A	B	C	Thickness [nm]	MSE
Base glass	1.529	1.532	0.05672	0.00343	-	2.456
PR06	2.262	1.945	0.03567	0.00235	10.00	2.543
PR21	1.994	1.910	0.04013	0.00262	82.63	3.454
PR30	1.959	1.898	0.02798	0.00148	137.97	3.214

The spectral dependence $n(\lambda)$ obtained in the range 350 – 1700 [nm] from the fitting procedure for the studied glasses are shown in Fig. 4

It may be observed in Fig. 4 that with the increase of the thickness of the ZrO_2 coating, its refractive index n is decreasing. The same dependences are reported by [28] and it is typical for a polymeric sol, where the polymers are weakly charged and the condensation rate is high.

The refractive index dispersions of investigated layers are quite similar to each other and exhibit a very high value, over 1.9, that is considerably higher than that obtained for standard optical glasses.

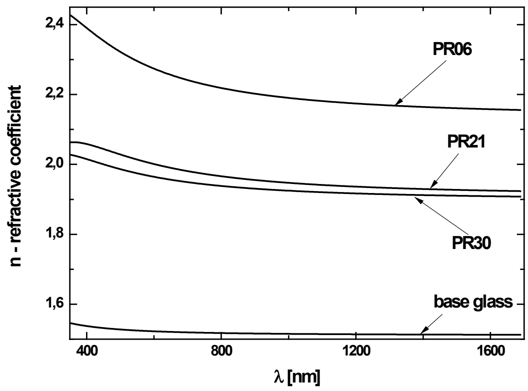

Fig. 4. Dispersion of the refraction coefficient of samples PR03, PR21 and PR30 obtained from elipsometric measurements

4. Conclusions

Zirconia-based coatings were successfully deposited on glass substrates. The study showed that by the sol-gel method it is possible to obtain layers with high adhesion to the substrate.

The relation between process parameters and thin layers features, such as thickness, was investigated. No cracks were observed below the critical layer thickness, which was determined for various zirconia coatings. On the basis of the transmittance studies, it was found that the layer with the highest hardness significantly reduced the transmission. The high refractive index coefficient indicate that the ZrO_2 film can be a potential optical coating material. The studies led to the selection of the optimal concentration of the zirconium sol and the conditions of heat treatment of zirconium layers.

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