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THERMAL AND MECHANICAL CHARACTERIZATION OF ZIRCONIUM BASED LPPS COATINGS ON GLASS

Marcin Drajewicz

Summary

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, LPPS (*Low Pressure Plasma Spraying*) method was used. The resulting materials were subjected to detailed examination of the thermal properties (cp-DSC, dilatometer, laser flash analysis), and mechanical tests (Vickers hardness and modulus of elasticity). The study showed that the obtained LPPS 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: plasma spray, zirconium oxide, thermal diffusivity, Vickers hardness, LPPS, layer

Charakterystyka właściwości cieplnych i mechanicznych warstw ZrO_2 wytworzonych na powierzchni szkła

Streszczenie

Właściwości mechaniczne szkła decydują o ich rozwoju i zastosowaniu w technice. Ograniczają jednak często wciąż ich właściwości użytkowe. Szczególnie dotyczy to właściwości, które zależą od składu fazowego i budowy warstwy wierzchniej szkła. Stąd poprawę tych właściwości szkła, zwłaszcza wytrzymałościowych, obecnie uzyskuje się przez modyfikowanie ich warstwy wierzchniej lub konstytuowanie nowej warstwy na podłożu szkła, m.in przez wytworzenie cienkiej warstwy tlenkowej metodami inżynierii powierzchni. W niniejszej pracy przyjęto założenie, że zastosowanie stabilizowanego tlenku ZrO_2 w procesie fizycznego osadzania z fazy gazowej w warunkach obniżonego ciśnienia pozwoli na wytworzenie stabilnej warstwy wierzchniej na podłożu szkła. Założono, że wytworzona warstwa zapewni również zwiększenie efektu umocnienia szkła krzemianowo – sodowo – wapiennego. Wykonano pomiary właściwości cieplnych i wytrzymałościowych oraz przeprowadzono analizy uzyskanych wyników.

Słowa kluczowe: natrysk plazmowy, tlenek cyrkonu, dyfuzyjność cieplna, twardość Vickersa, warstwa, metoda LPPS

Address: Marcin DRAJEWICZ DSc. Eng., Rzeszów University of Technology, The Faculty of Mechanical Engineering and Aeronautics, Department of Material Science, Powstańców Warszawy 8, 35-959 Rzeszów, e-mail: drajewic@prz.edu.pl

Introdaction

The mechanical properties of glass still determine its use in the art. The main factor limiting the performance characteristics are often still unsatisfactory mechanical properties. Improvement in these properties, in particular strength is currently achieved by modifying the surface layer of glass m.in by forming on the surface a thin oxide layer [1, 2].

The theoretical tensile strength of glass is approx. 7000 MPa for the clear glass without defects. In contrast, tensile strength of technical glass is 35-70 MPa, which is about 10% of its theoretical strength. It is characterized by the Griffith equation [3]. It depends primarily on the density of defects in the surface layer of glass – typically having a thickness of 1-10 microns [1, 3]. Thus, the strength properties of the glass are determined by the state of its surface and the density of defects in the surface layer. The improvement of the strength properties of the glass achieved a number of ways [4, 5, 6]. Bartholomew showed that the glass strength can be increased in the manufacturing process, or by modifying the surface layer. Many studies have shown [7] that flame polishing and chemical etching of the surface layer of these products is not very effective methods. They allow only temporary increase of the strength properties of glass – at a time of stress relaxation. Way more effective treatment is laser edge of the pane of glass [5, 8]. It shall also apply hybrid methods, including strengthening chemical connection – ion exchange and flame treatment. Glass is also strengthened in the manufacturing process by generating compressive stresses in the surface layer. The stresses in the surface layer of glass formed in the processes: the heat strengthening, ion exchange, glazing enamels or by forming the surface layer characterized by a lower coefficient of linear thermal expansion [9]. It was found that effective protection of the glass surface is not so modified surface layer having a thickness of approx. 30 μm [10].

Other methods leading to an increase in strength properties of the glass is applying to the surface an additional coating. It is assumed that the process for producing a protective coating are chemical methods of strengthening the glass surface. There is in fact the chemical reaction on the glass surface allows formation of the protective layer. Typical layers of protective coatings are sol - gel matrix coating of organosilanes and hybrid organic - inorganic [11].

Increasing the mechanical properties of the glass also achieved by formation on the surface of the oxide layer ZrO_2 [12, 13]. Zirconium oxide, in particular the polymorphic form of tetragonal structure, characterized by high values of elastic modulus (Young's modulus E) and good tribological properties [14, 15]. ZrO_2 oxide layer on the glass surface can be prepared by a variety of methods. One of the latest method is a plasma spray physical vapor deposition under reduced pressure (50÷200 Pa – LPPS, Ang. Low Pressure Plasma Spraying) [16, 17].

Analysis of literature data and own research indicates the possibility of increasing the effect of strengthening the particular types of glass used in photovoltaic cells and mobile phones. Good tensile strength is the basic criteria of the use of glass in this case. It adopted a hypothesis that applying a coating of oxide-stabilized ZrO_2 x nY_2O_3 in the process of physical vapor deposition under reduced pressure will enable the formation of a stable surface layer, which provides an increasing effect of the strengthening of a silica - soda - lime. Hence, the work attempts to develop a comprehensive process conditions plasma spraying under reduced pressure to produce a uniform layer of ZrO_2 x nY_2O_3. Significant in this respect was to investigate the thermal characteristics of the substrate. This will allow the expected mechanical and optical properties of the glass.

1. Research methods

Material for the study was a soda-lime-silicate oxide ZrO_2 stabilized with Y_2O_3. In order to develop a comprehensive selection criteria layer material and the conditions of the plasma spraying under reduced pressure to produce a uniform layer of ZrO_2 x nY_2O_3 glass was analyzed heat.

Studies on the thermal properties are an important area of study when considering the problems of heat transfer, wherein from the point of view of thermal conductivity is particularly important test coefficient of thermal conductivity, thermal diffusivity and specific heat of solid, liquid and gas. The thermal conductivity and thermal diffusivity of materials are important thermophysical parameters necessary to describe the heat transport of analyzed materials. These parameters are the basis for the implementation of accurate simulation, the distribution of the temperature field in the elements, such as electronics, energy turbines or other control devices.

It was chosen glass thickness of 4 mm formed by a float under the trade name Ultra ClearFloat Guardian, and glass Float Glass Company NSG / Pilkington. The chemical composition and the basic properties of the glasses are shown in Table 1.

Tab. 1. The chemical composition of industrial glass

Glass	Chemical composition of glass, weight %							
	SiO_2	CaO	Na_2O	MgO	Al_2O_3	K_2O	SO_3	Fe_2O_3
Guardian	73,20	11,25	15,10	0,06	0,15	0,04	0,17	0,01
NSG	72,60	8,40	13,9	3,90	1,10	0,60	0,20	0,11

To measure the specific heat (heat capacity) uses the differential calorimetry. During the measurement, consisting in the implementation of the program defined during the temperature rise, the differential heat flow between the test sample and the reference sample. The method of directly benefiting from the equation:

$$c_p(T) = \frac{HF}{m_0 \cdot \beta} \tag{1}$$

where: c_p – specific heat, kJ/(kg·K); HF – heat flow, kJ/s; m_0 – sample weight, kg; β – heating rate, K/s.

The accuracy of the direct method depends on the correctness of the calibration curve, the accuracy of weighing the samples: the test and reference and execution of the blank. The estimated uncertainty is approx. ±5%. Measurements of the specific heat c_p/DSC performed on a Differential Scanning Calorimetry F3 Jupiter Saturn Netzsch. Thermal diffusivity may be determined one of the experimental methods: batch or pulse based on the temperature dependence of time (the temperature history). In the group of laser methods of pulse outputs (LFM – Laser Flash Methods) method can distinguish axial impulse (LFMA) of one-dimensional heat flow along the axis of the disc-shaped sample. The energy source is a laser. The energy of the laser radiation absorbed by the front surface of the sample violates its thermal equilibrium. After some time the temperature of the whole sample are compensated. As a result of the absorption of the laser pulse suitably selected parameters, the subsurface layer of material is generated surfaced heat source.

Measurements of the coefficient of thermal diffusion are performed on cylindrical samples (pellets) placed in a corundum cylindrical holder. This is placed in the furnace and subjected to a precise heating process. Upon reaching the designated temperature, in the direction of one of the surfaces of the sample, sending the laser pulse, a portion of energy which leads to an increase in temperature. Preparation of temperature gradient in the thickness of the sample to activate the flow of heat towards the colder the surface, the temperature of which is measured as a function of time using the IR sensor. Measurements of diffusion coefficients is made for the device temperature Netzsch LFA 427.

Glass as amorphous materials characterized by isotropic properties. The thermal expansion of polycrystalline materials, and amorphous plastic examined by dilatometer. It is worth recalling that empirically determined linear coefficient of thermal expansion is characterized test material only in the temperature range in which the measurement was carried out [18]. Dilatometer is a device capable of registering the change in length of the sample tested material associated with changes in temperature. Dilatometric tests were performed on dilatometer Netzsch DIL 402C. Measurements were carried out in an atmosphere of helium. Test samples in the form of a rod with a length of 25 mm was heated at a rate of 5K/min to a temperature of 650°C. The coating on the substrate of soda - lime - silicate glass prepared by physical vapor evaporation using a plasma torch (PS-PVD). The study was conducted by means of a LPPS-thin film equipment located at the Materials Research Laboratory for Aviation Industry.

Studies layer hardness was carried out using Nano-Indentation Tester (NHT) CSM. The test apparatus allows precise registration of the load curve – the penetration depth of the indenter. Berkovich indenter used angle of the pyramid of 65° and maximum load 10 mN. Established speed load increase – 20 mN/min. Each of the samples was performed 30 imprints.

2. Results and discussion

The results of measurements of specific heat and thermal diffusivity of the glass Guardian and NSG shown in Fig. 1 and 2.

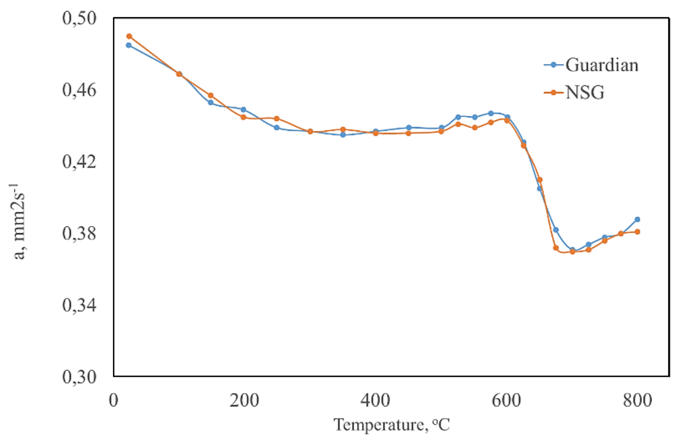

Fig. 1. Thermal diffusivity of the glass Guardian and NSG

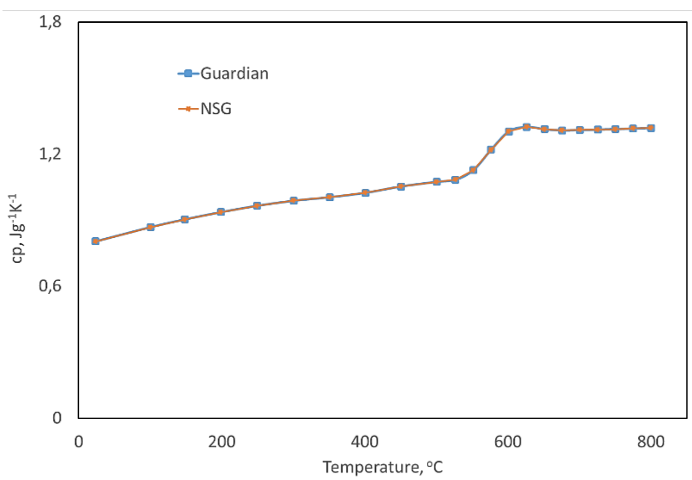

Fig. 2. The specific heat of the glass Guardian and NSG

Results of geometric changes glass samples Guardian and NSG in the range 20-650°C are shown in Fig. 3 and 4.

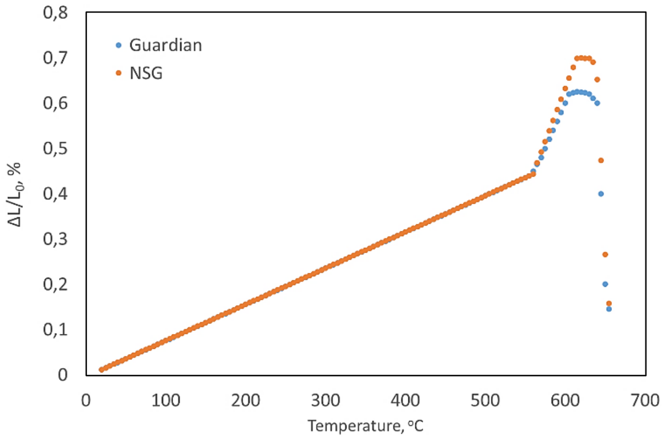

Fig. 3. Relative lengthening the float glass production Guardian and NSG

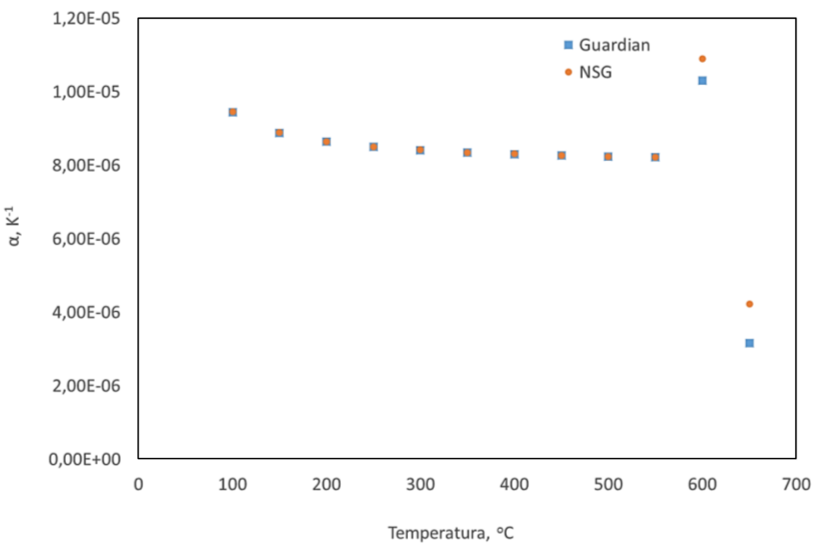

Fig. 4. Changing the linear coefficient of thermal expansion of float glass production Guardian and the NSG as a function of temperature

The values of T_g and the T_d of glasses float production Guardian determined from dilatometric curves shown in Table 2.

Tab. 2. The values of T_g and the T_d of glasses

Glass	T_g, ºC]	T_d, ºC]
Guardian	549.5	611.1
NSG/Pilkington	554.5	614.0

For isotropic bodies, which include soda – calcium – silicate glass, there are no differences in coefficient of linear thermal expansion depending on the direction of measurement, hence the assumption:

$$\beta_V \approx\sim 3 \cdot \alpha_L \tag{2}$$

Based on the assumption recorded by equation (2), the density of the glass as a function of temperature can be expressed as follows:

$$\rho_T = \frac{\rho_0}{(1 + 3 \cdot \alpha_L \cdot \Delta T} \tag{3}$$

where: ρ_T – the density of the glass at temperature T, g/cm^3; ρ_0 – density of the glass at a reference temperature, for example 200°C, g/cm^3; α_L – average coefficient of thermal expansion in the range ΔT; ΔT The temperature difference.

Density values were measured at 25°C on AccuPyc 1330 helium pycnometer from Micromeritics. The principle of operation of the apparatus is based on the use of gas to precisely determine the sample volume. The density of soda-lime--silicate glass in the range of 100-600°C was calculated according to equation 3. The results are shown graphically in Fig. 5.

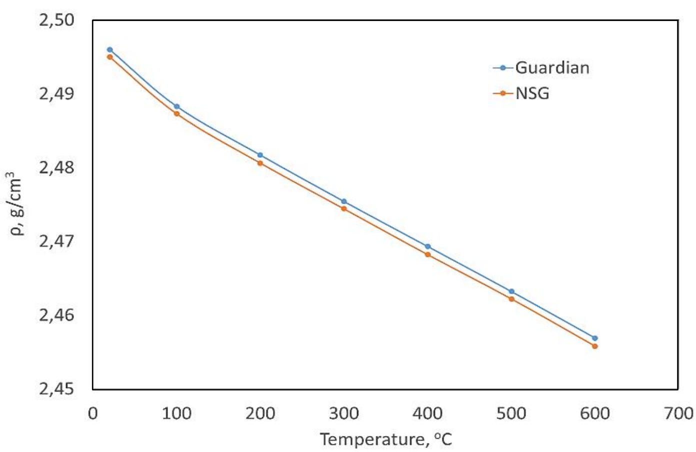

Fig. 5. Density of soda – lime – silicate glass in the range of 100-600°C

The relative change in the density range 20-600°C is approx. 1.7% for all tested glasses, so it is negligible in the calculation of the other properties of glass.

Determination of thermal diffusivity, density and heat capacity allows (according to Equation 3) knowledge of the thermal conductivity of the materials tested.

$$\lambda(T) = a(T) \cdot c_p(T) \cdot \rho(T) \qquad (4)$$

and (S) – heat diffusion coefficient, m^2/s; $c_p(T)$ – specific heat (heat capacity), J/(kg · K); $\rho(T)$ – the density, kg/m^3.

The values of thermal diffusivity and specific heat derived from direct measurements. Density at temperatures of 100-600°C was calculated based on density measurements at room temperature and a coefficient of linear thermal expansion in the range of 100-650°C. The values of thermal conductivity of soda-lime-silicate glass at temperatures of 25-600°C calculated from formula (4), for a constant value of the density or density as a function of temperature are summarized in Fig. 6.

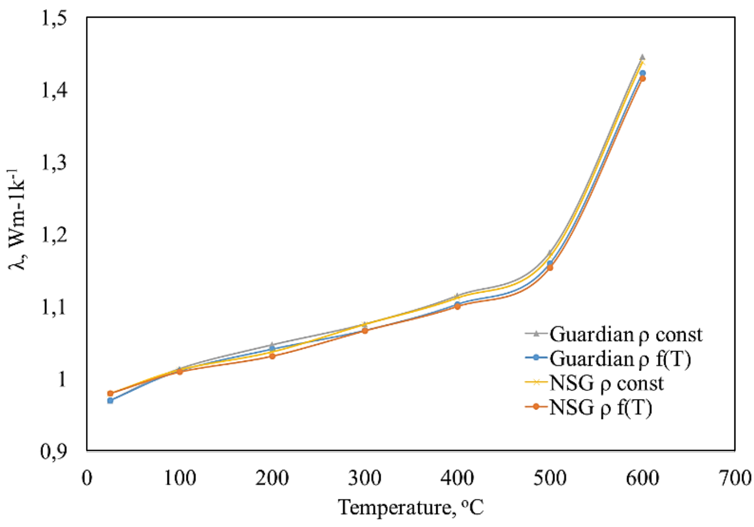

Fig. 6. Thermal conductivity of soda-lime-silicate Guardian and NSG glass at temperatures of 25-600°C

As a result of processes obtained glass with an oxide layer of ZrO_2, in which the measurements of hardness to glass of different thicknesses zirconia layer (sample PR1 (80 nm), PR2 (250 nm), PR3 (580 nm)) and the measurement results were averaged and are presented in Fig. 7.

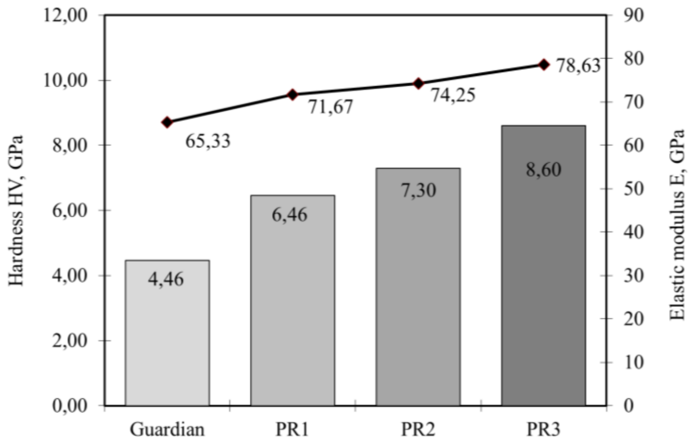

Fig. 7. HV hardness and Elastic modulus E
for glass Guardian – Base and glass PR1 – PR3

Studies have shown that the samples containing oxide ZrO_2 have a significant increase in hardness of the surface of the glass as compared to glass base (Guardian). The best results were achieved on samples of glass PR3 (hardness 8.60 GPa). Other samples were also characterized by a significant increase in the hardness of greater than about 50% of the hardness of the base glass.

3. Conclusions

Thermal properties: specific heat, thermal conductivity and thermal diffusivity have anomalous changes in the transformation. As is known, the transformation of glassy does not fulfill the criterion of thermodynamic phase transition of the first or second kind, and most often defined as "thermodynamic phase transition manifestation of the second type, which may not occur for reasons of kinetics. Therefore, the transition temperature varies with the cooling rate. Zirconia-based coatings were successfully deposited on glass substrates. The study showed that by the LPPS 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.

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