Study of optical and mechanical strengths of the glass composites with sol-gel films

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Abstract. Dependences of optical and mechanical strengths of glass composites with the drawn films upon the film thickness, particles packing density in a layer in the sol disperse phase and the particles diameter have been studied experimentally. We report that the laser ablation threshold energy density values decrease with the growth of the composites microhardness.

1. Introduction
The glass composites with the films drawn on the glass substrate optical and mechanical strengths dependence on the physical properties of such a composites studies have been fulfilled in the continuing of our works [1, 2]. Optical strength, as well as earlier [1], is meant as the probability of the lack of the breakdown at the sample surface for the set threshold energy density $F_{bn}$ of the film laser ablation destruction irradiated by the laser radiation pulse with the energy of 140 mJ and 20 ns time duration and mechanical strength is the composites microhardness $H$. Interaction of the laser radiation pulse of 20 ns duration can be reduced to material thermosplitting process that is similar to the process of the microhardness estimation by the method of a diamond pyramid cave-in.

This work goal is the glass composites with the drawn films optical and mechanical strengths dependences on the film thickness, particles packing density in a layer in the sol disperse phase and these particles diameter experimental studies.

2. Experimental samples and methods
Samples of $50 \times 50 \times 4$ mm³ in size from the glass plate substrate had the drawn two-component film of the $z\text{Me}_x\text{O}_y\text{TiO}_2$ system, where $z = 2$ or 10 wt %, and $\text{Me}_x\text{O}_y$ were the next: $\text{CuO}, \text{ZnO}, \text{CdO}, \text{SnO}$, $\text{Fe}_2\text{O}_3$. The chlorides or nitrates of the chosen metals and the titan tetraethoxide in the isopropanol were used for the sols preparation.

The chlorides or nitrates of copper, zinc, cadmium, tin and iron were dissolved in isopropyl alcohol, then the titan tetraethoxide and hydrochloric or nitric acid, of the same name with anion of the salt of metal used for the sol preparation were added to the solution. The total oxides mass content in the sol is of 5%. These solutions were maintained for maturing from 1 to 11 days before the films drawing. The drawing speed was constant and equal to of 5.8 mm/s.
After the film drawing on the substrate the sample was maintained on the air within 1 hour and was burned in the microwave furnace within 30 minutes.

The light transmission by KFK-3 device and the sol viscosity by the VPZh-1 viscometer experimental measurements results allowed to estimate the particles diameter in the sol disperse phase by Heller method [1] and the particles packing density in the film layer [1] was calculated by Einstein equation [3] proceeding from an assumption that the particles form of the sol disperse phase are close to the spherical.

The \( z\text{Me}_2\text{O}_y\text{-TiO}_2 \) composition films thickness \( h \) and refractive index \( n \) values were measured by the spectral ellipsometry with the HORIBA type Uvisel 2 apparatus.

The microhardness data for these composite samples were recorded by the indentation of the diamond pyramid method at the hardnessmeter Nexus 4504-IMP type with the strength of 100 g and loading time of 10 s.

For the films laser ablation experimental studies the measurements of the laser radiation threshold energy density of \( F_b \) values at which the film breakdown begins on the sample surface have been fulfilled. The laboratory laser ablation station for these measurements was described in detail in [1]. The YAG-Nd laser generated the pulses at the 1064 nm wavelength with time duration of 20 ns and pulse energy up to 150 mJ. This laser radiation was focused by a special objective on the composite sample surface. The breakdown phenomenon was fixed by the presence of the laser plasma plume light emission that was recorded by the FSD-8 type micro spectrometer. The laser pulse energy density changing in the range from 0.1 up to 150 J/cm\(^2\) was achieved both the objective focal length choice and the radiation weakening by the NS type calibrated neutral glass filters. The spectrometer regimes were operated by the PC and the PC standard codes were used for the station controlling and measurement results treatment.

The calibration experiments have been made at the FP-4 type PTFE target as in [1]. The probability curve generation for the laser breakdown demands to make not less than 20 shots at the fixed laser radiation pulse energy and to measure the number of the breakdown events on the target surface. All of the breakdown probability range with the values from 1 up to 0 has been consistently studied taking the new, smaller, energy density value and repeating this measuring process again at the new point on the target surface. This procedure includes the exact positioning and displacement of the target around the laser beam focus point. Such a way designed sample irradiation optimal layout was used in all further experiments. The threshold energy density \( F_b \) values have been taken from these curves for the equal experimental condition and the breakdown probability \( P = 0.5 \) [1]. These values can be served for the optical strength or durability dynamics studies.

3. Experimental results

The microhardness of the composites with various values of the film refractive index was studied at the first stage. The plots connecting the composites microhardness and the film refractive index values received from chloride and the nitrate containing precursors are given in figure 1.

These experimental results were approximated by the linear function. The results showed that composites microhardness values and the films refractive index values increase with the increasing in the particles packing density of the disperse phase in the layer. It is naturally as the material hardness increases with its density increasing and the film refractive index value is also connected with its porosity according to expression [4]:

\[
n_{\text{eff}} = n_1 - \Pi (n_1 - n_3) - (n_2 - n_3) \times f \left( \frac{P}{P_0} \right),
\]

where \( n_{\text{eff}}, n_1, n_2, n_3 \)—respectively the refractive indexes of the film, the material skeleton with the film adsorbed water and air; \( \Pi \)—the material porosity; function \( f(P/P_0) \)—the adsorption isotherm.
Figure 1. The plot of composites microhardness $H$ dependences on the film refractive index $n$ values: 1—chloride, 2—nitrate containing precursors.

The change of the film thickness favors to the $n$ and $H$ values increasing irrespective to the precursors type used for the sol preparation. Plot of the composite microhardness changing with the film thickness are exhibited in figure 2.

These experimental results were approximated by the linear functions for the films from the sols on the basis of the nitrate and chloride containing precursors respectively.

The refractive index increasing was connected with the weakening of the diffusion of the low-refracting oxides of silicon, sodium and calcium from a substrate into the film in the process of its thickness growth [5].
Table 1. The oxides constants in the additivity formulas for the glass CTE calculation by the Demkina method.

| Oxide  | $A_0 \times 10^7 \text{ }^{\circ}\text{C}^{-1}$ | $\varphi_0 \times 10^7 \text{ }^{\circ}\text{C}^{-1}$ |
|--------|---------------------------------------------|-----------------------------------------------|
| TiO$_2$| $-12$                                       | 0.11                                          |
| SiO$_2$| $30$                                        | $-0.075 \ (0.092)$                            |
| SnO$_2$| $-208$                                      | 0.68                                          |
| CaO    | $70$                                        | 0.54                                          |
| ZnO    | $-110$                                      | 1.50                                          |
| CdO    | $-160$                                      | 1.98                                          |
| CuO    | $-60$                                       | —                                             |
| Na$_2$O| $354$                                       | 0.42                                          |

The constants in the additive formulas for the coefficient of thermal expansion (CTE) $a_t$ calculation for the glasses by the Demkina method [6] have been fulfilled as

$$a_t = \Sigma b_0 \ (A_0 + \varphi_0 t),$$

where $A_0$ is the constant which is equal to the thermal expansion coefficient of this oxide at the $t = 0 \ ^\circ C$ temperature; $\varphi_0$—the oxide thermal expansion coefficient; $b_0$—the oxide concentration value in the volume ratio. These $A_0$ and $\varphi_0$ values have been determined by Demkina and Shchavelev for the 32 oxides and the fluorine of glass. Substituting them into the above formula it can be calculated CTE values of the glass have been calculated at any temperature with an accuracy of $\pm (2-3) \times 10^{-7} \ ^\circ C^{-1}$. The calculated results are given in the table 1. These data are attracted as according to [7] thin layer films received by the sol-gel chemical way are mainly amorphous and are close to the vitreous by its nature.

It is obviously from table 1 that the sodium, calcium and silicon oxides getting into the film from the substrate have the positive $A_0$ values, but the other oxides have the negative values of the $A_0$. It leads to the essential difference in CTE on the border of the section the film–the transitional layer and this difference increases with the increasing in the film thickness [7]. The stated hypothesis is one of the most probable. It is noticed that some films are so strained by the CTE difference that they become covered by cracks after heat treatment.

Figure 3 shows interrelation of $F_{bn}$ and $H$ values of the composites. The linear functions were chosen for these experimental results approximation for the films from the sols on the basis of the nitrate and chloride precursors respectively as earlier.

Rather low values of the approximation coefficients testify to the complexity of this interrelation which probably does not limited only by CTE difference. As experiments show the composites reflection coefficient at the 1064 nm laser radiation wavelength are made the very essential contribution to laser ablation destruction. The $F_{bn}$ values have the tendency to increase in the process of the reflection coefficient growth.

The laser ablation threshold energy density at the laser radiation pulse of 20 ns time duration decreases with growth of the composites microhardness that is the natural consequence of the stated earlier hypothesis. Comparison of the figures 2 and 3 shows that the microhardness grows with the film thickness increasing and CTE difference in the transitional layer–film at the same time increases. As a result the film intensity increases and it is required the insignificant threshold energy for its thermo splitting.

In general, the plot of figure 3 allows assuming that the sample laser ablation threshold energy density considerably depends on CTE of the layers which are formed in the film and on the composite reflection coefficient at the laser radiation wavelength.
Figure 3. The plot of composites laser ablation threshold energy density $F_{bn}$ dependences on the film microhardness $H$ values: 1—chloride, 2—nitrate containing precursors.

4. Conclusion

The following main conclusions are possible to draw from this work:

(i) The refractive index changing of the films drawn from nitrate and the chloride containing precursors is proportional to the composite microhardness growth.

(ii) The film thickness changing favors to increase of $n$ and $H$ values irrespective of the precursors type used for sol preparation. The refractive index increasing is connected with the weakening of the diffusion of the low-refracting silicon, sodium and calcium oxides from the substrate to the film but the microhardness increasing—with increasing in the CTE difference of the layers which are formed in the film.

(iii) The laser ablation threshold energy density values decrease with the growth of the composites microhardness. This phenomenon is explained from the position of the CTE difference of the layers which are formed in the film. The experimental result also shows that the composites reflection coefficient increasing at the 1064 nm laser radiation wavelength promotes to the laser ablation destruction threshold energy density growth.

References

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