STRESSES IN CHALCOGENIDE GLASSES ON ELASTIC AND VISCOELASTIC SUBSTRATES

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Abstract. The stresses in compositions of chalcogenide glasses with other materials are calculated. The calculations are performed in the approximation of infinite flat seals of glasses with elastic materials and other glasses. It is shown that the results of calculations can be used for choosing material compositions and conditions of their production and operation.

1. Introduction

Chalcogenide glasses are well-known materials with a unique combination of properties, such as the high radiation resistance, wide transmission band in the IR spectral range, reversible electrical switching and memory, and the ability to undergo structural transformations. Chalcogenide glasses have been predominantly used for recording and transfer of information in optics and for fabrication of elements of integrated circuits in electronics. Chalcogenide glasses in the form of layers, films, and coatings are compatible with different materials (metals, glasses, ceramics, polymers) and with each other, for example, in light guides (core and cladding) and buffer layers between an environment and active parts of devices.

As a rule, stresses exist in a composite consisting of two materials. This is an important factor that can affect the service reliability of the composite and the properties of its constituting materials. Let us consider a glass that is a component of an infinite flat seal with a particular material. If the second component of the seal is an elastic solid or another glass, the stresses can be estimated using well-developed methods for calculating stresses in similar seals. The aim of the present work is to estimate stresses in seals of chalcogenide glasses with other materials in the approximation of infinite flat seals formed by glasses with elastic solids and different glasses.

2. Calculation techniques

The computer programs were created for calculations stresses in glass-to-elastic body and glass-to-glass seals. These programs based on well-known methods of calculation stresses in such seals [1]. These programs were debugged and tested with the use of the data taken from papers devoted to calculation stresses in seals.

3. Results of calculations

In order to calculate the stresses in a seal under specific temperature-time conditions, it was necessary to determine the dilatometric curves of the seal components under these conditions. The calculations were performed under the assumption that the dilatometric curves of elastic materials should be unchanged. The dilatometric curves were calculated according to equations of Tool-Naraynaswamy
glass transition model represented in [2]. The necessary data for calculation dilatometric curves of chalcogenide glasses were taken from [3].

The stresses were calculated in the seals of some chalcogenide glasses with ceramic materials (Al₂O₃, MgO, ZrO₂), other glasses (silica glass SiO₂, window glass), metals (Al, Cu, Au), silicon and poly(styrene). In the calculations, it was assumed that the ratio between the thickness of the chalcogenide glass and the thickness of second seal component is equal to 1/10, which may correspond to the coating-substrate composite. As an example figure 1 shows the temperature dependences of the stresses in coating of As₂S₃ glass on different substrates during cooling. The maximum magnitude of the residual stresses 78 MPa was obtained for the As₂S₃-SiO₂ seal. By assuming that the ultimate adhesion strength of a coating to a substrate is equal to 100 MPa (the most typical value available in the literature), we can make the inference that the residual stresses in As₂S₃ coatings do not exceed the ultimate strength.

**Figure 1.** Temperature dependences of stresses in coatings of As₂S₃ glass on different substrates during cooling at a rate of 10 K/min. Substrates: (1) SiO₂, (2) Si, (3) ZrO₂, (4) Al₂O₃, (5) window glass, (6) Au, (7) MgO, (8) Cu, (9) Al, and 10 poly(styrene). The negative stresses are tensile stresses, and the positive stresses are compressive stresses.

The stresses in glass seals with other materials depend not only on the physical properties of seals components but also on another factors. The following factors were considered: temperature conditions of preparation and operation (cooling, heating, annealing), the ratio of coating thickness to the substrate thickness. Accomplished work demonstrates that calculation is an efficient method for evaluating the influence of different factors on the stresses.
Furthermore, we have calculated stresses in a number of glass-glass seals consisting of different chalcogenide glasses. The stresses were calculated upon cooling and heating at a constant rate in the seals for which the thickness ratio of components is equal to 1/1. The $\text{As}_2\text{Se}_3$-$\text{As}_2\text{S}_3$, $\text{TlAsSe}_2$-$\text{TlAsS}_2$ seals, and seals of the $\text{As}_2\text{S}_3$ glass with some glasses of the Ge-As-Se system were studied. The seals are characterized by different temperature dependences of stresses, and the residual stresses that differ by one order magnitude.

Figure 2 depicts the temperature dependences of the stresses in two seals of the $\text{As}_2\text{S}_3$ glass with Ge-As-Se glasses.

![Figure 2](image-url)

**Figure 2.** Temperature dependences of stresses in compositions of $\text{As}_2\text{S}_3$ glass with glasses of Ge-As-Se system during cooling and heating. Compositions: (a) $\text{As}_2\text{S}_3$-$\text{Ge}_{10}\text{As}_{10}\text{Se}_{80}$, (b) $\text{As}_2\text{S}_3$-$\text{Ge}_{20}\text{As}_{20}\text{Se}_{60}$. The cooling and heating rates are equal to 10 K/min.

The model calculations can be useful in choosing the technique for producing seals, in searching for optimum annealing conditions, and in predicting both the long term stability of seals and the properties of their components at high operating temperatures.

The calculations performed in this work are rather complex. In practice, as a rule, it is necessary to evaluate the possibility of producing a seal with the use of a small number of parameters for sealed materials and simple formulas for calculating stresses.

In practical work associated with annealing of glass-metal seals, the theory of instantaneous solidification has been used for estimating stresses without application of relaxation models. In the framework of this theory, it is assumed that stresses in a seal instantaneously relax above the glass transition temperature $T_g$, and do not relax at all lower temperature.

The formula for stress calculation has the form

$$\sigma = \frac{E_g}{1 - \mu_g} \cdot \frac{(\alpha_g - \alpha)}{(E_g d_g / E_d + 1)} \Delta T,$$

where $E_g$ is Young’s modulus, $\mu_g$ is Poisson’s ratio, $\alpha_g$ is thermal expansion coefficient, and $d_g$ is the thickness of the glass; $E$, $\alpha$, and $d$ are the parameter of elastic component; and $\Delta T = (T_g - T_{room})$. The
residual stresses calculated for the seals within the relaxation theory ($\sigma_{rel}$) and the theory of instantaneous solidification ($\sigma_{inst}$) for $\text{As}_2\text{S}_3$ glass are compared in Table 1. If $\text{As}_2\text{S}_3$–Al seal is excluded out of consideration, the average difference in percentage between the residual stresses $\sigma_{rel}$ and $\sigma_{inst}$ is equal to 6%. The theory of instantaneous solidification, on the whole, gives satisfactory result for seals with elastic substrates.

The theory of instantaneous solidification was used to estimate stresses in chalcogenide glass – elastic material seals formed by number of chalcogenide glasses. The calculation was carried out for forty glasses in the As-Se, As-S, As-Se-Tl, As-S-Tl, Ge-Se, and Ge-As-Se systems. The calculated data have demonstrated that the stresses in the seals are lower than the ultimate strength of 100 MPa. Therefore, it can be expected that the system consists of thin layer of chalcogenide glasses on elastic substrates should be stable.

**Table 1.** Residual stresses in glass seals with different materials according to the calculation within the relaxation theory ($\sigma_{rel}$) and the theory of instantaneous solidification ($\sigma_{inst}$)

|           | $\text{As}_2\text{Se}_3$ | $\text{SiO}_2$ | Si | $\text{ZrO}_2$ | $\text{Al}_2\text{O}_3$ | Window glass | Au | MgO | Cu | Al | Poly styrene |
|-----------|--------------------------|----------------|----|----------------|------------------------|--------------|----|-----|----|----|-------------|
| $\sigma_{rel}$ | -77 MPa                  | -73 MPa        | -59 MPa | -49 MPa        | -47 MPa                | -33 MPa      | -28 MPa | -25 MPa | 6 MPa | 7 MPa |
| $\sigma_{inst}$ | -82 MPa                  | -76 MPa        | -61 MPa | -50 MPa        | -47 MPa                | -31 MPa      | -25 MPa | -22 MPa | 3 MPa | 6 MPa |

**References**

[1] Scherer, G.W., Relaxation in Glass and Composites, N.Y., 1992, 332 p.
[2] Moynihan, C.T., Macedo, P.B., Montrose, C.J., et al., Structural Relaxation in Vitreous Materials, Ann. N.Y. Acad. Sci., 1976, vol. 279, pp. 15-35.
[3] Ananichev, V.A., Preparation of Chalcogenide Glasses and Investigation of Their Structure by Volume Dilatometry, Doctoral Dissertation, St. Petersburg: St. Petersburg State Polytechnical Univ., 2003