Characteristics of diffusion zone in changing glass-metal composite processing conditions

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Abstract. The influence of manufacturing technology on the characteristics of the glass and steel contact zone in manufacturing new structural material - glass-metal composite is studied theoretically and experimentally. Different types of structures in the contact zone and its dimensions affect the strength characteristics of the composite. Knowledge about changing the width of the glass and steel contact zone after changing such parameters of the technological regime as temperature, holding time and use of solders will allow one to control the structure and characteristics of the glass-metal composite. Experimental measurements of the width of the diffusion zone in the glass-metal composite for different regimes and their statistical processing according to the full factor experiment are presented in this article. The results of analysis of some mechanical characteristics of the diffusion zone are presented: microhardness and modulus of elasticity for samples, prepared according to different processing regimes.

1. Introduction

Technological features of manufacturing a new structural material based on glass and steel – glass-metal composite are considered in this article [1]. Experimental samples of a three-layer cylindrical tube (5154 aluminum alloy - aluminosilicate - 5154 aluminum alloy) [2] and a double-layer rod (steel (AISI 1010, AISI 1020) glass (borosilicate glasses, CGW-7052)) have been obtained [3], technological regimes and characteristics of the obtained samples are analyzed.

The temperature regime for manufacturing glass-metal composite includes: heating to a certain temperature; holding at this temperature and cooling. In this article, it is proposed to model the results of the third stage - the width of zone saturated with iron, as a consequence of diffusion processes. Conducting individual experiments and studying the theoretical foundations for obtaining junctions allow one to assume, that it is possible to identify main factors of technological process, which influence on diffusion: T is the maximum heating temperature, t is the holding time at the maximum temperature, and TO is the type of treating of connectable surfaces.

Describing the processes of glass-steel connection in individual experiments, the authors of this article tend to effectiveness of the theory of oxide compound [7]. This theory explains the mechanism of glass-steel connection through an oxide layer and is described by two stages: physical adsorption and wettability; chemical reactions and prolonged diffusion. To improve the interaction, a stable oxide
layer of wustite is created on steel surface by a special method. Wustite is well wetted and dissolves in the glass, helps the formation of a strong connection due to occurring of diffusion processes and the chemical interaction of metal oxides with glass components with the formation of a diffusion (transition) layer. The idea of additional treatment (after cold chemical treatment) of the connected surfaces with salts that improve the solubility of the oxide layer is checked in this article.

2. Results and Discussion
To study the influence of the width of bonding zone from temperature, time, and method of the surface treatment, the structure of glass-metal composite based on borosilicate glass and steel AISI 1020 manufactured according to different modes was experimentally studied. The sample is a composite cylinder with a glass core and an outer steel sheath. Two methods for treating the inner surface of steel cylindrical billets are considered: cold chemical treatment and solder treatment based on sodium tetraborate.

To study the structure of the glass and metal composite, a thin section was prepared (Figure 1), the microstructure was studied with a scanning electron microscope Hitachi S-3400N (Hitachi, Japan), equipped with EDS and WDX X-ray spectrum analysis detectors. Microscopic study was conducted in backscattered-electron mode (BSE, COMP) at various magnifications. Obtained X-ray spectrum analysis data show changing in the elemental composition along the line of investigation, starting from the light region of the metallic steel substrate, the metal-glass transition zone, and ending with the dark region of glass phase of the glass-metal composite. The width of diffusion zone was determined for each sample as the mean value of the five lines of variation in the concentration of iron in glass from maximum to zero, taking into account the measurement error (Figure 1).

![Analytical data of X-ray spectrum analysis with linear scanning (mass content of Fe) and a scheme for conducting a linear scan.

Experimental results of measurements of the width of diffusion zone under different regimes are presented in Table. 1.
Table 1. Experimental data.

| Temperature (T), °C | Without sodium tetraborate t=30,40,50,60 (min) | treating method t=100,120(min) | Sodium tetraborate t=40,60(min) | Sodium tetraborate t=100,120 (min) |
|-------------------|-----------------|-----------------|------------------|------------------|
| 750               | 79.6; 81.5(40)  | 85; 87 (100)    | 97; 95(40)       | 115.3; 98 (120)  |
| 800               | 106; 105 (30)117,2; 125,1 (60) | 110; 106; 113 (100) | 122; 136 (60) | 145.8; 135.2(100) |
| 850               | 12; 16 (30)22 (40) | 36; 34; 41 (100) | 132; 139 (60) | 151.2; 159.5(100) |

To process the experimental data (the construction of the regression model), a full factorial experiment of type $2^3$ was used, with a number of factors equal to 3 and a number of levels equal to 2. The number of experiments is $N = 8$. Three factors were considered as factors of optimization of the function $y$ (width of the diffusion zone): $x_1 = T$ (temperature), $x_2 = t$ (holding time), $x_3 = B$ (treating method - absence or presence of sodium tetraborate). Variants of the values of the levels of factors are given in Table 2.

Table 2. Options for determining the values of factor levels.

| Variants | The levels of factors | T, °C | t, min | B |
|----------|-----------------------|-------|--------|---|
| I        | –1                    | 750,800 | 30,40,50,60 (≤60) | a |
|          | +1                    | 850   | 100,120 (≥100) | b |
| II       | –1                    | 750   | 30,40,50,60 (≤60) | a |
|          | +1                    | 850   | 100,120 (≥100) | b |
| III      | –1                    | 800   | 30,40,50,60 (≤60) | a |
|          | +1                    | 850   | 100,120 (≥100) | b |
| IV       | –1                    | 750   | 30,40,50,60 (≤60) | a |
|          | +1                    | 800,850 | 100,120 (≥100) | b |

a) Without sodium tetraborate.
b) Sodium tetraborate.

Statistical processing of the experimental data was carried out in the following order: exclusion of differed data; determination of variance of optimization parameter; checking the homogeneity of variances; calculation of estimates of coefficients of the regression equation; checking the significance of regression coefficients, checking the adequacy of the model.

The Student's test was used to determine the error of parallel experiments, when checking for all variants, there were no differed data, so all values were left. The number of measurements for different points in the factor space (sets of values of factors) is different, so the hypothesis of homogeneity (equality) of the variances $H_0: \sigma_1^2 = \sigma_2^2 = \cdots = \sigma_K^2$ was tested using the Bartlett M-criterion. Dispersions of variants I-III are homogeneous, while the hypothesis of homogeneity for variant IV is rejected.
The results of constructing regression models for variants I-III are represented. There are significant coefficients at the significance level $\alpha = 0.95$ in the equations.

Option I: $t_{cr} = t_{0.95;22} = 2.074$. Significant coefficients: $b_0=98.128$, $b_1=-11.541$, $b_2=5.903$, $b_3=33.603$, $b_{13}=25.234$. The model looks like:

$$y = 98.128 - 11.541T + 5.903t + 33.603B + 25.234TB.$$  

(1)

Option II: $t_{cr} = t_{0.95;11} = 2.201$. Significant coefficients $b_0=89.444$, $b_1=-2.856$, $b_2=6.806$, $b_3=33.931$, $b_{12}=2.781$, $b_{13}=24.906$. The model looks like:

$$y = 89.444 - 2.856T + 6.806t + 33.931B + 2.781Tt + 24.906TB.$$  

(2)

Option III: $t_{cr} = t_{0.95;14} = 2.145$. Significant coefficients $b_0=104.855$, $b_1=-18.268$, $b_2=5.774$, $b_3=35.232$, $b_{12}=3.814$, $b_{13}=23.605$. The model looks like:

$$y = 104.855 - 18.268T + 5.774t + 35.232B + 3.814Tt + 23.605TB.$$  

(3)

Since the variances for variant IV are heterogeneous, the regression model for variant IV was not constructed. To check the adequacy of mathematical models (1) - (3), an analysis of variance was used. The adequacy of the model was checked using the Fisher test. Table 3 shows the results of checking the adequacy of models.

| Variants | Inadequacy | df | SS     | MS=SS/df | $F_{cal}$= MS/MS$_{er}$ | $F_{crit}$ | Inference |
|----------|------------|----|--------|----------|------------------------|-----------|-----------|
| I        | Inadequacy | 3  | 683.6637 | 227.8879 | 0.978 | 3.049 | Adequate |
|          | Error      | 22 | 5126.0925 | 233.0042 | - | - | - |
| II       | Inadequacy | 1  | 14.7730  | 14.7730  | 0.490 | 4.747 | Adequate |
|          | Error      | 11 | 331.3950 | 30.1268 | - | - | - |
| III      | Inadequacy | 1  | 159.2233 | 159.2233 | 3.530 | 4.600 | Adequate |
|          | Error      | 14 | 631.4192 | 45.1014 | - | - | - |

Analyzing the surfaces in Figure 2, it can also be noted that the values of the width of diffusion zone at $T = 1$ for (1) - (3) differ by not more than 10%, at $T = -1$ it makes sense to compare the surfaces by models (1) and (2) and (1) and (3), the difference is no more than 15% (Figure 2, b).

Figure 2. Graphical representation of regression models (1) - (3): a - without sodium tetraborate (B = -
Figures 3 and 4 show the results of measurements of the microhardness and modulus of elasticity for individual samples manufactured in different modes. Diagrams of average values of modulus of elasticity (Figure 4) in glass (G), diffusion zone (DZ) and steel (St) show that its values in the glass and diffusion zone at chosen intervals of changing of technological parameters does not depend on these parameters, for steel changing of modulus of elasticity does not exceed 15%. The dispersion of microhardness values (Figure 3) is more significant especially for the diffusion zone, in sample No. 7 the high value of microhardness in the diffusion zone is associated with the formation of the solid phase of fayalite in glass.

![Figure 3](image1.png)

**Figure 3.** a) Microhardness in HV (SHIMADZU DUH-211S): 1- material without treatment; 2- T = 740 °C, t = 40 min; 3-B, T = 740 °C, t = 40 min; 4-B, T = 740 °C, t = 120 min; 5-T = 800 °C, t = 30 min, 6- T = 800 °C, t = 100 min; 7-T = 850 °C, t = 30 min; b) Sample №7 after microhardness test.

![Figure 4](image2.png)

**Figure 4.** a) when indenting in GPa (SHIMADZU DUH-211S): 1- material without treatment; 2- T = 740 °C, t = 40 min; 3-B, T = 740 °C, t = 40 min; 4-B, T = 740 °C, t = 120 min; 5-T = 800 °C, t = 30 min, 6- T = 800 °C, t = 100 min; 7-T = 850 °C, t = 30 min; b) A diagram of modulus of elasticity of sample №4.

3. Conclusions

Obtained models (1) - (3) are adequate, and theoretically any of three models describes diffusion zone width variation with the regime parameters. The main conclusion, which follows from the analytical dependencies (1) - (3), graphically presented in Figure 2, lies in the fact that with increasing temperature, holding time and the presence of sodium tetraborate, the width of the diffusion zone can be made arbitrarily large. On the one hand, this is not in contrast with experimentally observed
diffusion processes with a similar technology for creating p-n junctions in semiconductors: by doping for a short time into the surface layer of the semiconductor and distillation - the distribution of the dopants along the thickness of the semiconductor [10]. Experimentally observed zone, containing iron in a semiconductor, grows with an increase of temperature and holding time. On the other hand, glass-metal composite manufacturing technology has significant differential characteristics because glass and steel connect in oxidizing atmosphere. When temperature increases, oxide layer on the steel without sodium tetraborate (B = -1) increases in thickness and changes its structure; these lead to reduction of the zone. That is why different tilting angles on the surfaces are associated (Figure 2, a, b). So, the upper temperature is limited to 850 °C (T = 1 for all models (1) - (3)).

Thus, on the basis of experimental measurements of width of the diffusion zone and statistical processing of data, analytical dependences of width of the diffusion zone on three parameters of technological regime have been obtained. These dependencies can be used in planning further experiments for manufacturing glass-metal composite and obtaining glass-steel connection.

The constructed models allow us to conclude that, with minimal values of factors such as temperature and holding time, the effect of steel, treated with sodium tetraborate, on the width of diffusion zone is not significant, so at the temperature of 750 °C and a holding time of ≤ 60 min, sodium tetraborate processing is not mandatory. But at higher temperatures and longer holding time, the difference in the width of diffusion zone in the treated samples is more than 100%. therefore at the temperature of 800 and 850 °C and holding time of > 60 min, the steel surface must be treated with sodium tetraborate.

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