Modeling of the kinetics of diffusion processes in the formation of a junction glass-steel

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Abstract. Basic types of structure of the contact zone of glass and steel as a result of long-term temperature processing, and mathematical models describing diffusion processes are explored in this article. The diffusion models of iron ions proposed in this paper agree with the experimental results. The effectiveness of the application of the diffusion coefficient in the Stokes-Einstein approximation is proved.

1. Relevance of research
Technological features of manufacturing of structural composites in which the metal layers alternate with the layers of glass imply the reduction of the glass layer by the metal shells, that additionally protect glass and prevent the formation of microdefects on the glass, and increase the static and dynamic strength of the glass layer and composite as a whole 1,2. The temperature regime for the production of a glass-metal composite has special features. For example, under different technological conditions, the quality of glass and metal contact zone can vary from a ”taut” connection to a vacuum-tight junction with a developed diffusion zone at the contact boundary. The modeling of concentration profiles in the diffusion layer will allow to predict the development of its structure and geometry and optimize the technological parameters of production. Most of studies of the diffusion of iron in glass are difficult to compare with the problem considered in this paper, with the exception of [2]–[6] works. A huge amount of work has been devoted to the mathematical modeling of diffusion processes, however, for each technological task, the problem of selecting the appropriate model and its correction remains topical in optimizing experimental studies. The purpose of this article is mathematical modeling of diffusion processes in the junction of glass and steel.

2. Research objectives
The obtaining of a glass-steel connection includes the formation of a complete physical contact and diffusion processes coming from the dissolution of the oxide layer on the steel in the glass and diffusion of iron in the glass. During the experimental studies, it was noticed that the reason and direct participant of the diffusion processes is the oxide layer on the steel surface [2]. Preliminary chemical treatment of the steel surface during further heating allows forming a wustite - FeO layer on its surface, and then the technology divides into two main directions: further joining without using solder and with solder based on sodium tetraborate \((Na_2B_4O_7 \times 10H_2O)\). There are two main types of the bonding zone. The main feature of the zone (I) is the presence of two
crystalline and amorphous phases different in concentration and structure: a small thickness (up to 5 micrometers) of crystalline phase with a high iron content, possibly this is a layer of fayalite $2\text{FeO} \cdot \text{SiO}_2$ and iron metasilicate $\text{FeO} \cdot \text{SiO}_2$, and a longer (up to 92 microns) amorphous phase with a lower iron content (Figure 1a). In case (II) only the amorphous phase (up to 252 μm) is observed, in this phase the iron concentration decreases uniformly in the direction from the joint zone (Figure 1b).

In some samples with the zone (I), conglomerates of insoluble iron oxides (most likely hematite $\text{Fe}_2\text{O}_3$) are seen (Figure 1a). All samples have a zone supersaturated with iron, which crystallizes upon further cooling. After the analytical processing of the results of spectral analysis this zone contains up to 40% of iron (point 3, Figure 1a), while the iron content of the nearby zone does not exceed 20% (point 4, Figure 1a). Samples with the zone (II) do not have similar crystalline phase, which is the result of preliminary treatment of the surface of steel with sodium tetraborate, which prevents the oxidation of the steel surface upon heating and accelerates the solubility of wustite in glass.

![Figure 1. Microstructure of two principal types of connection zone: (a) -I and (b) -II (Hitachi S-3400N), soldering temperature 800 °C, dwell time 100 minutes.](image)

Analytical processing of intensity profiles with linear scanning (Figure 2) allows to distinguish typical dependencies for different methods of surface treatment: type I-cold chemical treatment and type II- cold chemical treatment with application of sodium teraborate, to note their similarity and differences. Despite the similar nature of the concentration profiles and the mechanism of iron diffusion, the mathematical description of types I and II will be different. Samples of the I type has step-like zone due to the presence of an initially wider oxide layer than in type II, as a consequence, the diffusion mobility of iron ions in this layer is limited and, with insufficient dwell time, forms a saturated layer, which subsequently crystallizes upon slow cooling.

### 3. Mathematical modeling

In general, the diffusion process at the glass and steel connection zone in a glass-metall composite resembles the creation of p-n junctions with two isolated stages: by doping for a short time into the surface layer of the semiconductor with the formation of a thin surface layer enriched with dopants and distillation-the distribution of the dopants along the thickness of the semiconductor during long time (sometimes dozens of hours) [7]. The use of additional treatment with sodium tetraborate prevents the growth of the oxide on the steel and its phase change, the saturation of the glass melt occurs from a thin layer of wustite dissolving first in the solder and then
diffusing into the glass melt. The iron diffusion model for type II can be described by models, accepted in the theory of semiconductors, for example, as diffusion from an infinitely thin layer into a semibounded body with a reflecting boundary, which corresponds to the condition of the presence of an excess concentration of iron in a thin surface layer, which is redistributed throughout the volume, decreasing on the surface and continuously increasing in volume [8], the initial and boundary conditions of the given problem have the form

\[ t = 0 : \delta \to 0, C = C_0 \quad \text{for} \quad 0 \leq x \leq \delta \quad \text{and} \quad C = 0 \quad \text{for} \quad \delta < x < \infty, \]

\[ x = 0 : t > 0, \frac{\partial C}{\partial x} = 0, \]

where \( C \) is the mass concentration of iron, \( C_0 \) is the concentration of diffusing iron in the oxide layer at the initial time, \( \delta \) is the thickness of the oxide layer, \( D \) is the diffusion coefficient of iron in the glass melt. If the diffusion coefficient does not depend on \( x \) \( \left(\frac{\partial D}{\partial x} = 0\right) \), then equation

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D(x)\frac{\partial C}{\partial x}\right), \quad 0 < x < \infty, \quad t > 0, \]

taking into account the boundary conditions (1) and (2), has an analytic solution

\[ C(x,t) = \frac{q}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}, \]

where \( q = C_0\delta \) is the amount of substance concentrated at the initial time in a layer of thickness \( \delta \to 0 \). Formula (4) can be used to estimate the diffusion coefficient \( D \) from the available experimental data from the solution of the nonlinear equation

\[ \frac{C(x_{exp}, t_{exp})}{q} \sqrt{\pi Dt_{exp}} = e^{-\frac{x_{exp}^2}{4t_{exp}}}, \]

where \( t_{exp}, x_{exp}, C(x_{exp}, t_{exp}) \) and \( q \) are experimentally defined parameters.

The diffusion process for the I type zone can be described by the diffusion of iron oxide into a viscous glass melt, from the boundary \( \delta \), which characterizes the motion of a viscous melt
along the oxide layer. Then the mathematical model represents a boundary value problem that includes the diffusion equations in two layers:

$$\frac{\partial C}{\partial t} = D_1 \frac{\partial^2 C}{\partial x^2}, \quad 0 < x < \delta(t), \quad t > 0,$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_2 \frac{\partial C}{\partial x} \right), \quad \delta(t) < x < \infty, \quad t > 0,$$

with initial and boundary conditions:

$$t = 0: \delta(0) = \delta_0, \quad C = C_0, \quad \text{for} \ 0 \leq x \leq \delta_0 \quad \text{and} \quad C = 0 \ \text{for} \ \delta_0 < x < \infty,$$

$$x = 0: \quad t > 0, \quad \frac{\partial C}{\partial x} = 0,$$

$$x = \delta(t): \quad t > 0, \quad D_1 \frac{\partial C}{\partial x} \bigg|_- = D_2 \frac{\partial C}{\partial x} \bigg|_+ \quad \text{and} \quad C \bigg|_- = KC \bigg|_+,$$

$$x \to \infty: \quad t > 0, \quad C \to 0,$$

here $D_1$ and $D_2$ are the diffusion coefficients in the oxide layer and the glass, respectively, $K$ is the solubility constant (determined experimentally), and $\delta(t)$ is the moving boundary of the viscous glass melt.

The diffusion process involves the dissolution of the oxide layer in the glass melt and its diffusion deep into the glass, the diffusion coefficients will have different approximations: in the oxide layer $D_1$, the mutual diffusion coefficient will be assumed constant until some time at which the oxide layer completely "dopes" into the glass melt, and $D_2$ depends on the viscosity of the glass and related with the Stokes-Einstein relation [4]

$$D_2 = \frac{k_B T}{6 \pi r \eta(C)},$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $r$ is the radius of the particle, $\eta(C)$ is the viscosity of the glass, which depends on the glass composition and temperature.

To determine $\delta(t)$ it is proposed to consider a mechanical model of the motion of the boundary of a viscous glass melt in the oxide layer, by analogy with the model for determining the time of formation of physical contact in a cylindrical junction of glass with a metal proposed in work [9]. It is necessary to solve the problem of Reynolds on the deformation of a viscous (glass) layer enclosed between two cylindrical plates, one of plates is fixed, force $Q$ acts on the other plate.

Using the axial symmetry, the neglect of the acceleration of the particles in the viscous layer, the thickness of the metal plates, and the condition of constant motion of the upper plate make possible to rewrite the Navier–Stokes equations and the continuity condition as

$$\eta \frac{\partial^2 \nu_r}{\partial z^2} = \frac{\partial p}{\partial r}, \quad \frac{\partial p}{\partial z} = 0,$$

$$\frac{1}{r} \frac{\partial (r \nu_r)}{\partial r} + \frac{\partial \nu_z}{\partial z} = 0.$$

With boundary conditions

$$z = 0: \quad \nu_z = 0, \quad \nu_r = 0,$$

$$z = \delta: \quad \nu_z = \frac{\partial h}{\partial t} = \nu(t), \quad \nu_r = 0,$$
where $\eta$ is the coefficient of dynamic viscosity, $r$ and $z$ are the radial and axial coordinates of the layer particle, respectively, $\nu_r$ is the velocity of the viscous layer in the radial direction; $P$ is the pressure in the layer; $\nu_z$ is the velocity of the viscous layer in the axial direction; $\delta$ is the current thickness of the layer; $\nu(t)$ is the velocity of the upper cylinder in the axial direction, $R$ is the radius of the metal plates. The change in the thickness of a viscous layer is due to a change in its radius as $\delta = R^2 C / R$. The solution of the boundary value problem leads to a nonlinear integral equation

$$
\int_{\delta_0}^{\delta} \frac{\eta(\tilde{\delta})}{\delta^3} d\tilde{\delta} = \frac{2Q t}{3\pi R^4}.
$$

(13)

The dynamic viscosity depends on the concentration, i.e. from the thickness of the saturation of the oxide layer by the melt. Depending on the analytical task $\eta$, the equation (13) can be solved analytically in the case of an integrand integrable in elementary functions, or numerically.

4. Discussion

The results of determining the experimental diffusion coefficients from formula (5) are shown in Figure 3 on the right. In Figure 3 on the left there are the experimental concentration profiles of iron for different technological regimes for samples of the II type, soldering temperature $850^\circ$C.

![Figure 3](image)

**Figure 3.** Experimental curves: a) the concentration distribution of iron for different dwell time: 1 - $t=30$ minutes, 2 - $t=60$ minutes, 3 - $t=100$ minutes; b) the diffusion coefficient: 1, 2, 3 - the experimental data by formula (5) corresponding with experimental curves of concentration 1, 2 and 3 (a), 4 - diffusion coefficient with approximation of the dependence of viscosity on the concentration of iron oxides by formula (12).

The numerical solution of problems (1)–(3), (6)–(13) has no special features, in this paper the numerical implementation was carried out using the implicit difference scheme, the sweep method and the quasilinear approximation of the diffusion coefficients from the time step [10]. There are a few studies about iron-containing glasses, in the calculations we use the approximation of the dependence of viscosity on the concentration of iron oxides proposed in work [4]. Comparing the
diffusion coefficients calculated by formula (5) with the aid of experimental iron concentration profiles and using of formula (12) where the dependence of the viscosity of glass depends on the concentration of iron in it [4] for samples of type II (Figure 3b), it can be stated that the diffusion coefficient calculated from the Stokes–Einstein relation is not only qualitatively, but also quantitatively close to the experimental curves, so the usage of it for calculating the iron concentration in samples of type II is justified. Figure 4 presents the results of numerical calculations of the concentration profiles of iron from the models: (1)–(3) for type I with the approximation of the diffusion coefficients according to the formula (5) (Figure 4a) and (6)–(13) (Figure 4b).

![Figure 4](image)

**Figure 4.** Concentration distribution of iron in samples: a) type II: 1- D=const [3], 2 - D by formula (12), 3 - D by formula (5); b) type I, D by formula (12) for different dweld time: 1 - t=40 minutes, 2 - t=60 minutes, 3 - t=100 minutes.

### 5. Conclusion

It is noted that the reason and direct participant of the diffusion processes in the welding of glass and steel is the oxide layer on the steel surface. The kinetics of the diffusion zone formation significantly depends on its characteristics and dwell time at the welding temperature. Depending on the technological regime, there are two main types of the connection zone structure. The results of calculations for the proposed models for each type are consistent with the experimental data. The model (6)–(13) is interesting and new. This model proposes a mechanical description of the motion of the boundaries of a viscous melt into an oxide layer. It is shown that the approximation of the diffusion coefficient by the Stokes–Einstein relation agrees with the experimental data, it is possible to state the relevance of studies about the dependence of the viscosity of glass on the concentration of metals in it for describing the diffusion processes in glasses.

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