Technological aspects of glass matrix production of temperature-resistant sitall coatings based on secondary industrial products

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Abstract. The paper considers technological aspects of the production of glass matrices of heat-resistant sitall coatings for the protection of nichrome alloys obtained on the basis of the RxOy - Al2O3 - SiO2 - TiO2 system (R = Li+, Na+, K+, Mg2+, Ca2+, Ba2+, Fe3+, Mn4+) using secondary raw materials are considered. The results of experimental studies of the synthesis and physico-chemical properties of matrix glasses for slag-and-metal coatings are presented.

1. Introduction

The current level of development of production and operation, in one way or another, is associated with the wide use of various metal elements that determine the exceptional properties of metals and metal structures [1-10].

With all the objective advantages of metals as a material, they also have significant disadvantages. The latter are due to the specific structure of the atom and the resulting chemical properties. In other words, the extremely important physical properties of metals for humans also have an objective disadvantage, due to their chemical properties. We are talking about such a widespread and already well-studied chemical phenomenon as corrosion, which causes the destruction of metal structures, tools, apparatuses, and products [1, 3-10].

In fact, metal corrosion minimizes all of the above qualities. Complex processes, which include corrosion, are especially dangerous also because they are almost invisible visually at the initial stages. This circumstance in some cases can pose a serious threat not only to individual elements and structures, but also to the life of a person or many people, depending on the location of corrosion.

As it is known, one of the most critical and important technological aspects of creating heat-resistant sitall coatings for high-temperature protection of nichrome alloys is, first of all, the synthesis of their glass matrices [11]. At present, when obtaining new materials, the use of secondary raw materials is extremely relevant, due to the urgent need for greening the environment and developing resource-saving technologies. When conducting experimental studies, well-known methods were used [12, 13].

The synthesis of matrix glasses for slag-metal coatings was carried out on the basis of the MgO – Al2O3 – SiO2 - TiO2 system, modified with the following oxides: Li2O, MgO, V2O, ZnO, TiO2, as well as the introduction of secondary raw materials into the charge [14-17].

The main requirements for the glass matrix of heat-resistant sitall coatings are:
- during heat treatment, the glass matrix must have the ability to form a sitall structure with the formation of stable crystal phases;
- the resulting glass matrix must have high thermomechanical properties [18-20].

2. Experimental method
To establish the optimal synthesis temperature, the prepared charge was melted at different temperatures. The glass was boiled at a temperature of 1350 ... 1370 °C with an exposure time of 2.5...3 hours. The synthesized glasses were cooled in a form of heat-resistant steel.

To study the structure and properties of the obtained glasses in the initial and heat-treated states, their powders were prepared, obtained as a result of grinding on rollers in porcelain drums. The fineness of the grinding was controlled by sieving through a sieve №0063 (10000 otv/sm²).

The main criterion for the possibility of using glass as the basis of heat-resistant coatings is the compliance of the TCLR of the glass and the substrate. In this regard, the dilatometric properties of the synthesized glass matrices were studied using well-known methods. The values of the dilatometric properties of glasses based on technogenic raw materials were determined on a DKV-4 quartz dilatometer. Taking into account the above requirements for the glass matrix of heat-resistant coatings and the value of TCLRH20N80 = 156∙10⁻⁷ K⁻¹, it should be noted the following: experimental glasses are quite acceptable for TCLR glass matrix of heat-resistant slag-and-metal coatings. It is known that the properties of heat-resistant metals are primarily determined by the ratio of the microcrystalline phases formed as a result of chemical treatment and the remaining vitreous phase. Thus, the study of the crystallization ability of the studied glasses, the modes of heat treatment, the determination of the composition and structure of the crystallizing phases, and the establishment of the conditions for the formation of the sitall structure are of exceptional importance. The crystallization capacity of the glass under study was determined by the method of mass crystallization. The glass samples were placed in alund crucibles in a furnace and kept for 30 minutes at the temperature of the experiment. Crystallization was carried out in the temperature range of 300... 800°C. After that, the samples were removed from the furnace, cooled in air, and analyzed [1].

3. Results and discussion
The results of determining the crystallization capacity of glasses are presented in Table 1.

| Table 1. The results of determining the crystallization capacity of glasses. |
|---------------------------------------------------------------|
| Name of the glass | 300…400°C | 400…500°C | 600…700°C | 700…800°C |
| 1 (VPAP) | ![1-1](image) | ![1-2](image) | ![1-3](image) | ![1-4](image) |
| 2 (Slag of The Novocherkassk SDPP) | ![2-1](image) | ![2-2](image) | ![2-3](image) | ![2-4](image) |

*Symbols: 1-1, 1-2; 2-1, 2-2-no signs of crystallization; 1-3; 2-3-the spread of crystallization over the entire volume of the glass (opalescence); 1-4; 2-4-conditionally complete volume crystallization, the degree of crystallization is 60-90%.
It is revealed that the experimental glasses have a sufficiently high crystallization capacity, which ensures the production of a sitall structure.

The density of all glasses after heat treatment increases in the range of 330... 770°C, which is in good agreement with the theoretical provisions in the field of sitallizable glasses.

Based on the experimental determination of microhardness, it can be concluded that the hardness of the glass after sitallization is significantly higher than before heat treatment. This is due to the release of crystalline phases in them, which have a high hardness. Due to the fact that the obtained sitals have an increased microhardness, they have a high mechanical strength and can be used for further research. The results of testing of samples of metals based on glass No. 1 are presented in Table 2.

As a result of the determinations, the thermal stability of the sitals was $\Delta T=800-22=778°C$. The percentage of damaged and undamaged samples was 20: 80.

**Table 2.** Results of determining the heat resistance of glass No. 1, heat-treated at a temperature of 770°C.

| № of the model | Model heating temperature in the furnace, °C | Water temperature in the reservoir, °C | Holding time in the drying cabinet, min. | Model damage |
|---------------|---------------------------------------------|----------------------------------------|------------------------------------------|--------------|
| 1             |                                             |                                        |                                          | No           |
| 2             |                                             |                                        |                                          | No           |
| 3             |                                             |                                        |                                          | Is there     |
| 4             |                                             |                                        |                                          | No           |
| 5             |                                             |                                        |                                          | No           |
| 6             | 800                                         | 22                                     | 12                                       | No           |
| 7             |                                             |                                        |                                          | Is there     |
| 8             |                                             |                                        |                                          | No           |
| 9             |                                             |                                        |                                          | No           |
| 10            |                                             |                                        |                                          | No           |

Based on the results of the study, it can be concluded that the obtained sitals have an increased heat resistance, which is characteristic of heat-resistant slag metals.

To obtain heat-resistant sitals, it is necessary that the glass matrices have a certain phase composition and a microcrystalline sitall structure. In order to achieve high thermomechanical properties, a high Al$_2$O$_3$ content of VPAP is introduced into the glass, which, along with Li$_2$O, ZnO and TiO$_2$, contributes to the formation of a fine-grained bulk microcrystalline structure of the glass. At the same time, it is possible to reduce the temperature of coating formation to 950 - 1050°C, which is favorable for the operation of nichrome alloys of the X20H80 grades. To establish the heat treatment regime and identify the optimal composition of glass №1, thermographic studies were carried out in the temperature range of 20...900°C [3-5].

DTA allows you to identify the temperature intervals of crystallization and the temperature of possible step processing as glass matrix. The nature of the thermogram allows us to judge the formation of crystalline phases. The correct choice and precise compliance with the heat treatment regime is of exceptional importance in sitall technology, as it allows you to:

a) ensure the formation of the necessary crystal phases in the glass matrix in an optimal ratio with the residual glass phase;
b) implement this process in the shortest possible time.

On the thermogram of sample № 1 (based on the VPAP) (Figure 1) there are the following exothermic maxima, °C: 330; 430;680; 770, and endoeffects, °C: 130; 370; 490; 560; 725; 780°C. The last, pronounced minimum indicates the melting of the glass.
Based on the obtained data, it can be concluded that the two-stage heat treatment of glass for the purpose of forming a sitall structure includes two stages of heat treatment, the temperatures of which are as follows:

I – $t_1 = 330^\circ C$, $t_2 = 430^\circ C$
II – $t_1 = 330^\circ C$, $t_2 = 680^\circ C$
III – $t_1 = 330^\circ C$, $t_2 = 770^\circ C$, where:

$t_1$ is the temperature of the pre-crystallization processes; $t_2$ is the temperature of the formation of the crystal phases. The holding time at each heat treatment stage is 1 hour. Observed endoeffects, $^\circ C$: 370; 49; 560; 725, 780 - they will play a positive role in the further synthesis of glass-crystal coatings. The endoeffect of $880^\circ C$ corresponds to the temperature of the beginning of softening of the glass matrix of the coating. The thermogram of model № 2 (based on Novocherkassk SDPP slag) (Figure 2) shows the following exothermic maxima, $^\circ C$: 135; 330; 440; 605; 735, and also endoeffects, $^\circ C$: 350; 475; 670; 790. The last, pronounced minimum indicates the beginning of deformation of the glass, followed by melting.

Based on the obtained data, it can be concluded that the two-stage heat treatment of glass for the purpose of forming a sitall structure includes two stages of heat treatment, the temperatures of which are as follows, $^\circ C$:

I – $t_1 = 330$, $t_2 = 440$
II – $t_1 = 330$, $t_2 = 605$
III – $t_1 = 330$, $t_2 = 735$, where

$t_1$ is the temperature of the pre-crystallization processes; $t_2$ is the temperature of the formation of the crystal phases. The holding time at each heat treatment stage is 1 hour. The observed endoeffects, $^\circ C$: 
350; 475; 670°C; 790°C will play a positive role in the further synthesis of glass-crystal materials with a sitall structure. The endoeffect of 790°C corresponds to the softening temperature of the glass.

In the two-stage mode adopted in industry, the main amount of the crystal phase should fall out when the temperature rises from \( t_1 \) to \( t_2 \). At the same time, sufficient deformation stability of the product is ensured by reinforcing the softening amorphous phase with a rapidly increasing amount of the crystalline phase. The duration of this stage is limited by the kinetic possibilities of the crystallization process, depending on the chemical composition of the glass.

### 4. Conclusions

As a result of the determination of the crystallization capacity of the glass under study by the mass crystallization method, it was revealed that the experimental glasses have a sufficiently high crystallization capacity, which ensures the production of a sitall structure.

Experimental determination of microhardness showed that the hardness of the glass after metallization is significantly higher than before heat treatment.

The determination of the heat resistance of the studied glasses revealed that the obtained sitals have an increased heat resistance, which is characteristic of heat-resistant slag metals.

The production of heat-resistant metals is possible with a two-stage heat treatment of glass. The necessary deformation stability of the product is formed by reinforcement softening of the amorphous phase by rapidly increasing amounts of the crystalline phase.

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