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DETERMINATION OF THE INFLUENCE OF TEMPERATURE, CONCENTRATION OF FERRIC OXIDES AND OXIDATIVE CONDITIONS OF GLASS BOILING ON THE DISPLACEMENT OF THE EQUILIBRIUM OF FERRIC OXIDES $Fe_2O_3 \leftrightarrow FeO$

The object of research is the state of equilibrium of ferrum(II) and ferrum(III) oxides in glass melts at temperatures of 1000–1400 °C, welded in oxidizing, neutral and reducing conditions with a content of ferrum oxides up to 1.5 %. This problem is relevant in the following aspects.

The first aspect of this problem is the unwanted coloring of the glass: FeO colors the glass blue, and Fe_2O_3 – yellow. The combined presence of ferrum(II) oxide and ferrum(III) oxide determines the gradations of glass shades that fall on the green spectrum.

The second aspect concerns the thermophysics of processes of boiling glasses containing iron oxides. Ferrum(II) oxide causes a strong absorption band of infrared radiation in the region of 1.1 μm. This becomes an obstacle to the volumetric heating of glass in the processes of cooking, forming, and annealing.

The third aspect of the problem concerns the structure of glasses and glass-crystalline materials with an increased content of iron oxides. Iron oxides significantly affect the processes of glass structuring, as ferrum(III) oxide is a typical network former, and ferrum(II) oxide is a typical modifier.

The state of $FeO \leftrightarrow Fe_2O_3$ equilibrium in glass is significantly influenced by the glass cooking environment, the total amount of iron oxides, and the temperature of the melt. The glass brewing environment has the greatest influence on the balance of iron oxides in the glass. The share of FeO oxide in the total amount of iron oxides ($FeO+Fe_2O_3$) increases sharply when moving from an oxidizing medium to a neutral one and then to a reducing one. During thermostating at a temperature of 1400 °C, the proportion of FeO in the glass increases by 1.4–1.7 times during cooking in an oxidizing environment, by 1.2–1.3 times in a neutral environment, and by approximately 1.1 times in a reducing environment. At the same time, this growth is more noticeable in glasses with a lower iron content.

Thus, the equilibrium state of $FeO \leftrightarrow Fe_2O_3$ in glass significantly affects the technological and operational properties of silicate melts and the final glass. The ratio of formed oxides of trivalent and divalent ferrum was studied by chemical (titrometric) analysis.

The research results can be used in practice to develop the composition of glasses with an increased content of iron oxides.

Keywords: *iron oxides, equilibrium state, redox potential, glass boiling, chemical analysis.*

1. Introduction

The so-called «iron in glass problem» has always existed in traditional glassmaking. Industrial glass is made, as a rule, from quarry raw materials (sand and limestone), which contain a certain amount of iron compounds. Even small impurities of which can radically change the spectral-optical characteristics of glass. Therefore, for industrial glasses, the content of iron oxides is limited to wt. %: 0.012–0.025 [1].

In silicate melts, divalent and trivalent ferrum is always in equilibrium. The Fe^{2+} ion has a strong absorption band in the near-infrared range, while Fe^{3+} absorbs mainly in the ultraviolet range. The color of glasses containing ferrum oxides in low concentrations can vary from blue-green to yellow-brown depending on the content of divalent and trivalent ferrum [2]. Such coloring of glass products is undesirable in most cases.

The study of the equilibrium between FeO and Fe_2O_3 in the melt, depending on its composition and temperature,

showed that as the temperature increases, the equilibrium shifts towards the formation of ferrum(II) oxide. At 1320–1410 °C, iron(II) oxide is contained in the melt by 50 % more than at 1230–1320 °C. With an increase in the content of silica and alumina in the melt, the equilibrium of the reaction shifts towards the formation of ferrum(II) oxide, and with an increase in the content of MgO – towards ferrum(III) oxide [3].

In addition, the balance of $Fe_2O_3 \leftrightarrow FeO$ in silicate melts affects the structure of the glass. Iron oxides, depending on the valence state of iron, play a dual role in glass: mesh former (Fe^{+3}) and modifier (Fe^{+2}) [4]. The Fe^{3+} ion is in the glass in tetrahedral coordination to oxygen and can replace silicon in the structure of anions and ensures the structural integrity of the vitreous body. In addition, an increase in the concentration of Fe_2O_3 leads to the appearance of Fe–O–Si bonds, which indicates the depolymerization of the glass network. The Fe^{2+} ion in glass has octahedral oxygen coordination and acts as a typical glass modifier [5–7].

The concentration of ferric ions and their redox state significantly affect the course of glass crystallization. In some cases, crystallization can occur spontaneously. The presence of Fe^{2+} causes glass crystallization faster and more significantly than Fe^{3+} [8]. This is due to the role of Fe^{2+} modifier, which will be able to diffuse and stimulate crystallization, while Fe^{3+} plays the role of network former and is less mobile. Ferrous iron ions can lead to the formation of magnetite, which, being the first to crystallize from a silicate melt at temperatures below 1300 °C, increases its heterogeneity and increases viscosity [9]. During the crystallization of iron-containing glasses, hematite (Fe_2O_3) or magnetite Fe_3O_4 crystals are formed, which give the glass magnetic properties due to the presence of clusters or crystals with magnetic properties [8].

Thus, it can be noted that a large number of properties of glass melts and finished glass will depend on the balance of iron oxides. First of all, these properties will significantly depend on the coordination of iron cations, their concentration, redox conditions of glass boiling, and temperature [4, 10–13]. However, the processes of chemical transformation and the conditions of coexistence of iron oxides in industrial glass production are practically not investigated. This especially applies to the heating and melting stages of the charge containing oxidants and reductants. The strong absorption band of FeO at $\lambda = 1.1 \mu m$ significantly reduces the effective thermal conductivity of glasses at cooking, production and forming temperatures, which must be taken into account when developing the appropriate temperature parameters [10, 14].

Another problem is that it is difficult to separate the amount of iron oxides in melts at different temperatures, so their content is often calculated as Fe_2O_3 (more often) or FeO. Due to these reasons, the data of different authors on the study of the viscosity of melts containing iron oxides and belonging to the same systems often do not coincide and often cannot be used to develop the compositions of iron-containing glasses and predict their properties [15].

Thus, the study of the influence of the content of iron oxides in glass, temperature and redox processes of cooking iron-containing glasses to ensure the optimal ratio between FeO and Fe_2O_3 in glass within technologically effective limits is an urgent task.

The aim of research is to identify the influence of temperature, concentration of iron oxides and oxidative conditions of glass making on the shift in the equilibrium of iron oxides $Fe_2O_3 \leftrightarrow FeO$. This will make it possible to predict the properties and develop new technologies for cooking glasses with an increased content of iron oxides.

2. Materials and Methods

The basis of the composition of the glass was the composition of sheet glass of the leading glass manufacturers, produced by the float method. Quantitative average statistical composition of sheet glasses is given in Table 1.

Table 1

Quantitative composition of industrial glasses obtained by the float method

Oxide	SiO_2	Na_2O	CaO	MgO	Al_2O_3
Statistical average content, wt. %	72.4	13.8	8.9	3.6	1.3
Maximum average statistical deviation, wt. %	+1.03	+1.54	−2.07	−0.81	+0.83

Iron oxides are an undesirable impurity in sheet glass. The average statistical content of iron oxides (in terms of Fe_2O_3) in such glasses is 0.1 %, and the maximum deviation does not exceed 0.025 %.

Glass, the composition of which is presented in the Table 2, was used for the experiments.

Table 2

Composition of experimental glass

Oxide	SiO_2	Na_2O	CaO	MgO	Al_2O_3	Σ
Oxide content, %	72.5	13.9	8.8	3.5	1.3	100

The batch was prepared from chemically pure reagents: amorphous silica (SiO_2), sodium carbonate (Na_2CO_3), calcium carbonate ($CaCO_3$), magnesium oxide (MgO) and aluminum oxide (Al_2O_3). In addition, a certain amount of ferrum(III) oxide (Fe_2O_3) was added to the charge for further study of the equilibrium state of ferrum oxides ($Fe_2O_3 \leftrightarrow FeO$), which is established in the glass. The content of Fe_2O_3 in the experimental glasses was: 0.25, 0.5, 1.0, and 1.5 % (by mass). Glass cooking was carried out in fireclay crucibles with a capacity of 200 ml in a laboratory gas furnace at a temperature of 1500 °C in oxidizing, neutral and reducing environments. Oxidation-reduction conditions for cooking glass were set by adjusting the air-gas ratio.

The equilibrium conditions of iron oxides were studied on samples thermostated for 10 hours at temperatures of 1000, 1200, and 1400 °C. Then the samples were sharply cooled to fix the equilibrium state of iron oxides in the glass. Glass without thermostating was also used to compare the properties.

The quantitative composition of oxides of trivalent and divalent ferrum was studied according to the method described in [3] with some changes. This method makes it possible to separately determine the amount of FeO and Fe_2O_3 in vitreous and glass-crystalline materials. The essence of the method is to dissolve glass in hydrofluoric acid and determine the Fe_2O_3 content in the resulting solution using the Trilon B titrometric method in the presence of the sodium sulfosalicylate indicator. Then, after introducing a strong oxidant into the solution, FeO oxidized to Fe_2O_3 is similarly titrated.

Pieces of iron-containing glass were ground in an agate mortar. A fraction of glass powder $\alpha \le 0.1$ cm was selected for research. A weight of glass weighing (m) 0.2 g was transferred to a polyethylene glass and moistened with hot water. Then 3–4 ml of hydrofluoric acid (HF) was added and the glass was completely dissolved. The polyethylene glass was placed in a water bath and kept for 3–6 min. until the glass is completely dissolved. After complete decomposition of the glass sample, 3–4 g of boric acid (H$_3$BO$_3$) was poured into a polyethylene beaker to bind excess HF. The contents of the beaker were stirred with a glass rod and transferred into a glass beaker with a volume of 100–150 ml. At the same time, pH=1–3 is set in the solution. 2.5 g of sodium sulfosalicylic acid powder was added to the hot solution. The solution acquires a pink-purple color. The sample was titrated with a 0.01 N Trilon B solution until discoloration. The spent volume of Trilon B (V_1) corresponds to the content of Fe$_2$O$_3$ in the glass.

After titration, 1.5 g of ammonium persulfate powder ((NH$_4$)$_2$S$_2$O$_8$) was added to the still hot solution to oxidize FeO to Fe$_2$O$_3$. At the same time, the solution again acquires a color from pink to intense purple. The colored solution was titrated with 0.01 N Trilon B solution until discoloration. The volume of Trilon B (V_2) corresponds to the content of FeO in the analyzed sample.

Calculation of the content of Fe$_2$O$_3$ and FeO in percent (%) was calculated according to the formulas:

$$\omega\left(\text{Fe}_2\text{O}_3\right) = \frac{V_1 \cdot T \cdot 100 \cdot K}{m},$$

$$\omega\left(\text{FeO}\right) = \frac{V_2 \cdot T \cdot 0.9 \cdot 100 \cdot K}{m},$$

where V_1 – the amount of 0.01 N Trilon B solution used for Fe$_2$O$_3$ titration, ml; V_2 – Trilon B solution used for the titration of FeO, oxidized with ammonium persulfate to Fe$_2$O$_3$, ml; T – Trilon B titer, expressed in terms of Fe$_2$O$_3$ (for a 0.01 N solution of Trilon B T=0.0004); K – the coefficient of normality of Trilon B solutions; 0.9 – the conversion factor from Fe$_2$O$_3$ to FeO; m – the weight of the glass weight, g.

To estimate the influence of the amount of iron oxides in the glass, the environment and the cooking temperature, the mass fraction of FeO in the total amount of oxides was determined by the formula:

$$\omega\left(\text{FeO}\right) = \frac{m\left(\text{FeO}\right)}{m\left(\text{FeO} + \text{Fe}_2\text{O}_3\right)},$$

where ω – the mass fraction, %; m – mass, g

3. Results and Discussion

Studies of the FeO↔Fe$_2$O$_3$ equilibrium have shown that the mass fraction of FeO oxide in the total amount of iron oxides (FeO+Fe$_2$O$_3$) increases sharply when moving from an oxidizing medium to a neutral one and then to a reducing one (Fig. 1, group of curves 1, 2, 3 and Fig. 2, groups of curves 1, 2, 3). At the same time, the transition from an oxidizing to a neutral environment for cooking glass leads to an increase in the mass fraction of FeO by approximately 2 times. And when transitioning from a neutral environment to a reducing environment, it increases by 2 or more times, respectively. Such a shift

in the Fe$_2$O$_3$↔FeO equilibrium is explained by the magnitude of the redox potential of the reaction.

The influence of the total content of oxides in the glass on the state of equilibrium is shown in Fig. 1. An increase in iron in the range of 0.25–1.5 % (by mass) in all cases leads to a decrease in the proportion of FeO (the equilibrium shifts to the right). This effect is more noticeable under conditions of relatively low total content of iron oxides. The asymptotic nature of the curves in the region with the maximum ferrum content indicates the stabilization of the FeO fraction, and the equilibrium state in general, at higher values of the total iron content than in the experiment.
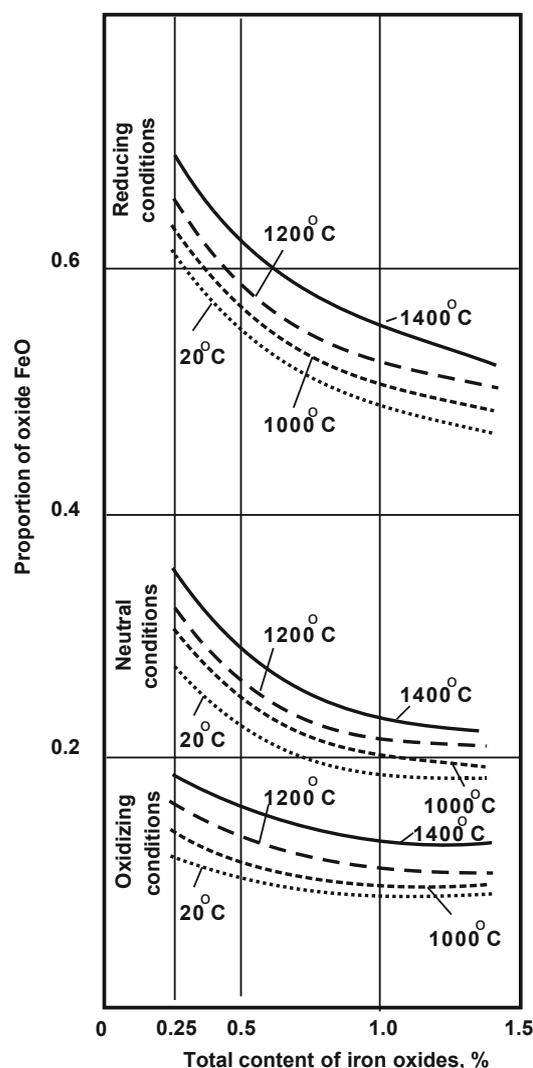

Fig. 1. The influence of the redox environment on the state of equilibrium of iron oxides depending on their content in the glass

The effect of temperature on the state of equilibrium is shown in Fig. 2. In oxidizing, neutral, and reducing environments, as the temperature rises to 1400 °C, the proportion of FeO in the glass increases:

– when cooking in an oxidizing environment – 1.4–1.7 times;

– in a neutral environment – 1.2–1.3 times;

– in a reducing environment – approximately 1.1 times.

At the same time, this growth is more noticeable in glasses with lower iron content.
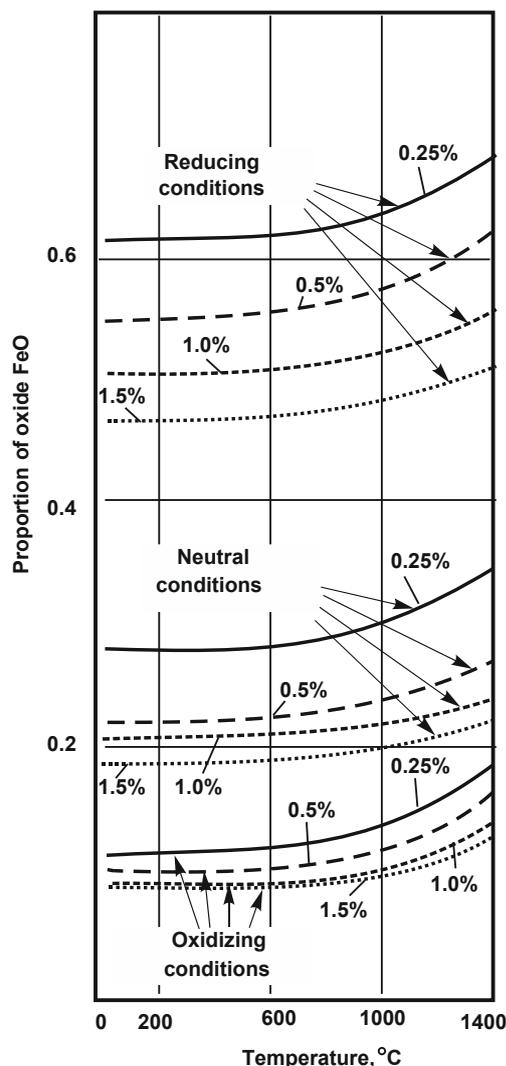
Fig. 2. Effect of temperature on the state of equilibrium of iron oxides

The equilibrium shift of $Fe_2O_3 \leftrightarrow FeO$ in the glass melt with increasing temperature occurs towards the formation of ferrum(II) oxide, which corresponds to Le Chatelier's principle. Since the oxidation reaction of FeO to Fe_2O_3 is exothermic, as the temperature rises, the equilibrium in the system shifts towards the endothermic reaction.

The influence of these three parameters on the state of equilibrium can be illustrated by the following diagram:

$FeO \Leftrightarrow Fe_2O_3$

strengthening of oxidizing conditions$\Rightarrow$

strengthening of recovery conditions$\Leftarrow$

increase in $FeO+Fe_2O_3$ content$\Rightarrow$

temperature rise$\Leftarrow$

Thus, for an accurate assessment of the properties of iron-containing glasses, it is necessary to take into account the concentration of iron oxides, the redox environment, and the temperature at which the glass is cooked. Since a significant number of properties of glass melts and finished glass will depend on the balance of iron oxides.

The limitation of the study is that the results were obtained only for silicate glasses of the SiO_2–Na_2O–CaO–MgO system with a total content of ferric oxides of 0.25–1.5 % in the temperature range of 20–1400 °C.

The conditions of martial law in Ukraine affected the time management of research and increased the time it took to conduct it.

The obtained results will be used to carry out research on high-temperature spectroscopy of iron-containing glasses and the development of glass compositions with satisfactory technological properties, having increased contents of iron oxides.

4. Conclusions

Thus, the conducted studies confirm that an increase in the temperature of the melt shifts the $FeO \leftrightarrow Fe_2O_3$ equilibrium towards the formation of ferrum(II) oxide.

An increase in the content of iron oxides from 0.25 to 1.5 % leads to a shift in the $FeO \leftrightarrow Fe_2O_3$ equilibrium towards the formation of ferrum(III) oxide.

Boiling glass under oxidizing conditions shifts the $FeO \leftrightarrow Fe_2O_3$ equilibrium towards the formation of ferrum(III) oxide, and boiling under reducing conditions – ferrum(II) oxide.

As the temperature rises to 1400 °C, the proportion of FeO in the glass increases by 1.4–1.7 times when boiled in an oxidizing environment, by 1.2–1.3 times in a neutral environment, and by approximately 1.1 times in a reducing environment. At the same time, this growth is more noticeable in glasses with lower iron content.

The results of the work can be used in practice for the development of the composition of glasses and vitreous materials with special properties, since the FeO/Fe_2O_3 ratio significantly affects the color of glass, its thermal, technological and operational properties, as well as the processes of structure formation in glass.

Also, the research results can be used to predict the properties and develop technology for cooking glasses with an increased content of iron oxides.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship, or any other, that could affect the study and its results presented in this article.

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Data availability

The manuscript has no associated data.

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