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DEVELOPMENT OF THE COMPOSITION OF SHEET GLASS WITH A LOW CONTENT OF AL_2O_3

In this work we present the results of the research on the development of new formulations of sheets of glass with low Al_2O_3. The study of the main indicators of the crystallization and properties, the data obtained in the calculation of the temperature dependence of the method M. Okhotin and technological indices proposed by "Emhart" provided arguments for selection of experimental glasses for float sheet glass.

Introduction. At present thermally polished sheet glass is produced in the Republic of Belarus at a single enterprise – JSC "Gomelsteklo". The modern line, put into operation in May 2010, achieved planned targets of production of about 25 million m^2/year, and started to produce sheet glass 2–12 mm at nominal value at least 70% of brand M1.

14–15 million m^2/year of sheet glass is an annual consumption in the Republic of Belarus and the volume of exports of this glass is approximately 10–11 million m^2/year, the main consumers being the CIS countries (Russia, Ukraine), the Baltic States, where there is lack of quality sheet glass.

The second float line, similar in construction to the first one, with a capacity of about 780 tons / day by glass mass is planned to be introduced in 2013 at JSC "Gomelsteklo". This product is intended only for the foreign market, where there are favorable conditions for JSC "Gomelsteklo".

Due to the increase of the enterprise production capacity by 2 times in the same manner in comparison with the current situation, its demand for raw materials will increase. In general, the problem of providing JSC "Gomelsteklo" with basic raw materials is solved except feldspar supplied by Vishnevogorsky Mining and Processing Plant (GOK, Russia). This component of the batch, although it belongs to low-tonnage, is a scarce raw material, and its delivery to JSC "Gomelsteklo", according to the administration GOK, in the next 2–3 years can not be substantially increased. Feldspar or other suppliers does not meet the technical requirements or lose economically.

Hence the need for a substantial reduction in the content of Al_2O_3 in the glass composition of the sheet, the source of which is the feldspar. Thus, it is necessary to take into account the following consequences: the increased tendency to crystallize, the change of physico-chemical properties of the glass, as well as the temperature characteristics, determining the mode of its melting and forming. To neutralize the consequences of reducing the content of Al_2O_3 in the glass sheet it is required to change the concentration of other basic oxides (SiO_2, Na_2O, CaO), primarily magnesium oxide, which has a positive effect on the crystallization stability, increases surface tension and improves the chemical resistance of the glass [1].

Results of the research and discussion. Based on the above, 15 experimental glass compositions were designed, in which the reduction of Al_2O_3 was compensated by increasing the MgO from 2.7 to 5.3 wt. % with simultaneous variation of the concentration of oxides SiO_2, CaO, Na_2O.

The properties of the synthesized experimental glasses were compared with the characteristics of the glass of the industrial composition of "Gomelsteklo" (composition № 1) obtained under the same conditions.

The comparative visual evaluation of the samples revealed that all the glasses are boiled thoroughly at a maximum temperature 1520 ° C, and lack of fusion and knag are absent, and the glasses have a small amount of gaseous inclusions in the form of a bubble with a diameter of about 0.3–1.5 mm.

When defining the properties of experimental glass, particular attention was paid to the crystallization ability. This is because the crystallization – highly undesirable phenomenon in the manufacture of sheet glass. We should take into account the danger of crystallization while cooling the boiled glass mass in the pool and head sections of a float bath. The crystallization of glass leads to mass flaw (defect) and is not permitted by the standards governing the quality of sheet glass.

The crystallization properties were studied by a method of gradient crystallization in a range of temperatures 645–1100°C (1 hour exposure). The temperatures of the upper and lower limit of crystallization were determined as well as the width of the secure forming interval corresponding to the temperature difference between the beginning of the forming ($T_{lg\eta=2.5}$) and the upper limit of crystallization temperature (U_{LCT}).

The evaluation of the crystallization ability (Table 1) shows that composition № 5 has the largest safe interval of forming followed by No.15, 2, 14, 1. respectively.

During the transition to the glass of other composition the upper limit of crystallization temperature increases up to 1100° and the safe interval of forming decreases. It has been established that the substitution of Al_2O_3 in the glass composition by MgO to 0.6 wt. % Al_2O_3 content does not cause a sharp deterioration in their ability to crystallization.

Table 1

Evaluation of the crystallization ability of experimental glass

No. of composition	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
U_{LCT}, °C	1015	965	–	1080	957	1055	1100	1100	1100	1100	1100	1057	1042	987	949	1073
L_{LCT}, °C	906	824	–	844	835	810	868	833	840	850	876	876	884	866	840	905
lgη = 2.5	1110	1107	1103	1100	1111	1109	1107	1105	1108	1104	1102	1100	1105	1099	1093	1088
Safe interval of forming, °C	95	142	–	20	154	54	7	5	8	4	2	43	63	112	144	15

Thus, according to the evaluation of melting and output characteristics as well as the results of determining the ability of the crystallization, glass compositions No. 2, 5, 14 and 15 are more suitable for producing a sheet of float glass, resulting in their choice for further research.

To determine the temperature dependence of the viscosity of experimental glass at the range of 10^2–10^{13} Па · с M.V. Okhotin method was used, and the temperature corresponding to the viscosity of 10 and 10^{14} Па · с was determined with the help of Fulcher – Tamman equation [2]. The graphic dependence of viscosity on temperature of experimental glass is shown in Fig. 1.

The analysis of graphic dependences lgη = $f(T)$ of the experimental glasses (Table 1) shows that their character is almost identical. The largest deviations are observed only at low temperatures (500–600°C, Fig. 1, a) and high temperature (900–1480°C, Fig. 1, c) range of the viscosity dependence.

On the basis of the viscosity curves, the values of characteristic temperatures, that are important for the technological process of production of float glass, were determined:

– melting temperature corresponding lgη = 10;
– temperature of the beginning of forming corresponding lgη = 2.5;
– temperature of Littleton corresponding lgη = 6.6;

– upper and lower temperatures of annealing;
– glass transition temperature corresponding lgη = 12.3.

According to the data presented in Table 2, the reduction of the total content of SiO_2 and Al_2O_3 by substituting them by oxides CaO and MgO causes the decrease of melting temperature by 30°C, which will provide fuel savings during melting, forming temperature – by 17°C and a lower annealing temperature – by 10°C. The remaining characteristic temperatures change very little.

To assess the characteristics of the glass the so-called "technological indexes" proposed by Emhart, often serve as criteria for their technological efficiency:

1) relative forming speed (RMS, %). At values RMS > 100% glass is considered to be suitable for forming;

2) processability index of WR, °C determines a forming temperature range;

3) relative length of glass WRI, °C determines a temperature interval of the form fixation. For most industrial glass compositions WRI> 170 ° C;

4) glass crystallization index of DI, °C. At values DI> 0 we can ignore the probability of crystallization of glass during production. When DI <0 we should consider the possibility of crystallization of glass during the forming process.

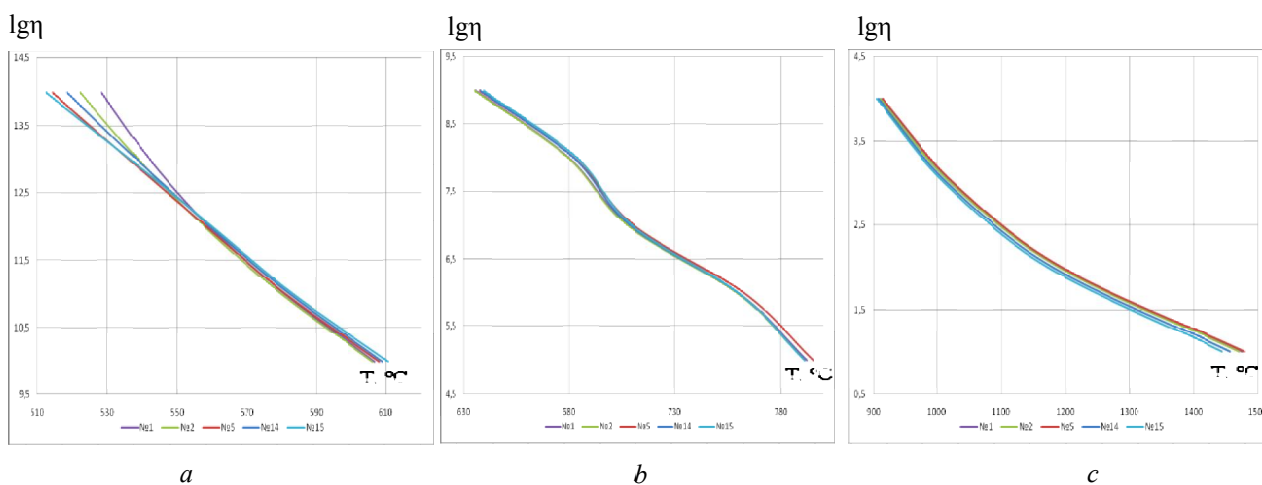Fig. 1. Temperature dependence of the viscosity of experimental glass at the range of:
a – low temperature (lgη = 10–14); b – medium temperature (lgη = 5–9);
c – high temperature (lgη = 1–4)

According to the calculation results (Table 3) it is evident that all five compositions are suitable for highly productive forming (RMS> 108%), have a fairly wide range of working status (WR varies from 364 to 381°C) and low tendency to crystallize in the process of developing (DI> 0 varies from 4.6 to 9.4°C).

From these data it follows that :

– the change in a chemical composition of the sheet glass (reduction of Al_2O_3 due to other oxides) slightly reduces the relative rate of forming products. Glass composition No. 1, in which the content of Al_2O_3 and SiO_2 are maximum, has the highest rate of forming;

– all the compositions under study have a wide enough interval of shaping. It should be noted that the substitution of Al_2O_3 in the glass composition by MgO reduces to some extent the value of this parameter;

– the temperature interval of the form fixation (WRI) when replacing Al_2O_3 in the glass composition by MgO increases slightly, resulting in the decrease in the rate of hardening of the glass;

– the index of crystallization also increases, indicating the increase in the crystallization stability when replacing Al_2O_3 by MgO.

The study of physical and chemical properties of the selected glasses was carried out: TFLE, density, micro-hardness, chemical resistance, according to which the property values of experimental glasses vary within a small range and are characteristic of sheet glass (Table 4). It should be noted that glass No. 2, 5, 14 and 15 correspond to hydrolytic class III, however, a decrease in the content of Al_2O_3 composition leads to some reduction of their hydrolytic stability.

One of the most important indicators of sheet glass is a light transmission index. The results of its definitions are presented in Fig. 2.

The analysis of graphic dependences showed that the experimental sheet glass have typical absorption bands in the visible (380–420 nm) and infrared areas of the spectrum (1000 –1100 nm), due to the presence of Fe^{3+} and Fe^{2+} ions in the glass composition, which provide the coloration of sheet glass.

Table 2

Evaluation of the crystallization ability of experimental glass

No. of compo-sition	Temperature of melting glass, °C	Temperature of forming, °C	Temperature of Littleton, °C	Upper temperature of annealing, °C	Glass transition temperature, °C	Lower temperature of annealing, °C
1	1476	1110	729	559	554	535
2	1471	1107	728	558	552	531
5	1480	1111	731	559	552	525
14	1458	1099	729	560	553	528
15	1445	1093	730	560	553	525

Table 3

Technological indexes of experimental glass

No. of composition	Technological indexes			
	RMS, %	WR, °C	WRI, °C	DI, °C
1	110	381	175	4.6
2	109	379	176	5.8
5	108	380	179	9.4
14	109	370	176	5.7
15	109	364	176	6.4

Table 4

Properties of experimental glass

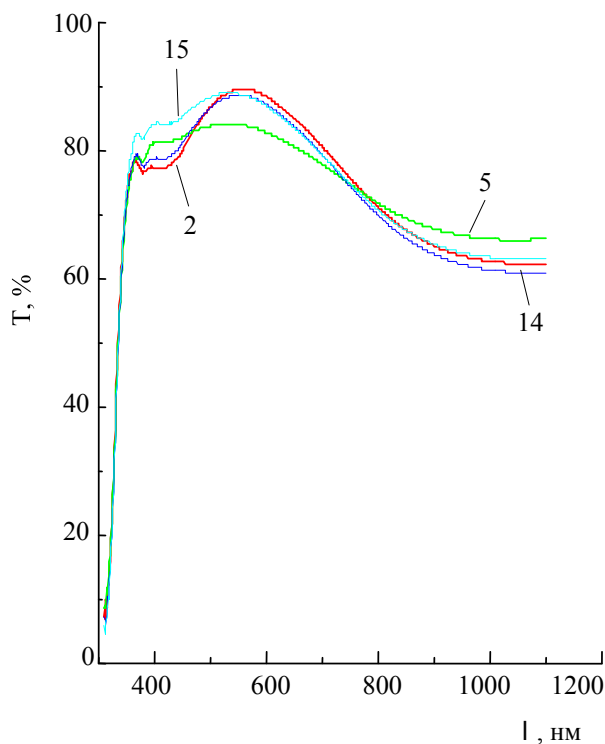| Properties		No. of glass composition				
		2	5	14	15	1
TFLE ($a \cdot 10^7$, K^{-1})	experimental	84.7	83.8	87.6	87.8	90.3
	calculated	91.3	90.6	91.8	92.7	
Density of glass, kg/m³	experimental	2479	2468	2479	2487	2496
	calculated	2493	2492	2500	2504	
Micro-hardness, MPa		5864	5761	5701	5688	5850
Amount of 0.01 n. HCl used for titration, ml		0.8	0.9	1.3	0.9	0.8
Hydrolytic class		III	III	III	III	III

Fig. 2. Light transmission of experimental glass

The observed differences in the glass in the process of light transmission in the visible and infrared areas are due to the different quantitative ratio of Fe^{3+} и Fe^{2+} ions. For glass compositions No. 5 and 15 the form of the light transmission curve is flatter in comparison with that for glass No. 2 and 14.

This circumstance is due to the increased number of Fe^{3+} ions, which absorb in the visible range of the spectrum, and the decrease in the number of ions Fe^{2+}, which accounts for the absorption maximum in the IR range of the spectrum.

The visible light transmittance index reaches maximum values for glass No. 15 and 2.

Conclusion. Thus, as a result of investigations of the crystallization ability, technological parameters and physico-chemical properties it was possible to reveal the ability to reduce the content of Al_2O_3 in the composition of sheet glass by 25–35% on condition of compensation of arising negative effects through the optimization ratios of oxides (MgO, SiO_2, Na_2O, CaO). Compositions No. 2 and 15, in accordance with a set of characteristics, best meet the requirements for float glass, which makes them effective for testing under conditions of JSC "Gomelsteklo".

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