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PRODUCTION OF TOUGHENED SHEET GLASSES OF THIN NOMINALS

An experimental apparatus for forming thin nominals glass by vertical drawing has been developed. The character and duration of transients in the area of sheet glass molding with thickness less than 2 mm in the stability of their geometric parameters and physicochemical properties have been researched. The time-temperature regimes of drawing of thin nominals sheet glass have been determined. It was found that their molding should be carried out in the temperature range of 840–850°C (glass viscosity $10^{4.8}$–10^5 Pa · s), since the detaching effect of surface tension forces does not lead to significant narrowing ribbon of the glass. According to the parameters of glass surface quality, glass drawn in this temperature range resembles float glass to some extent. However, it is characterized by the lower thickness (0.5 mm). The temperature increase to 900–950°C (in the active forming zone) causes the decrease of the surface quality and a significant narrowing of the glass ribbon at the expense of forces of surface tension. Being formed in the temperature range of 800–750°C on the roller drawing device the glass ribbon requires more effort high. It reduces the efficiency of the process.

The researches of toughness of thin nominals sheet glass demonstrate that the low-temperature ion-exchange treatment in the KNO_3 melt at the temperature of 400–500°C causes significant increase of strength, microhardness and glass heat resistance. The concentration of K^+ ions exercises a decisive impact on glasses properties in this temperature range. Being processed the K^+ ions diffuse to a depth of 10–15 μm of a surface layer of the glass and cause high values of compressive stress.

Key words: vertical drawing, sheet glass hardening, low temperature ion exchange, potassium nitrate, diffusion, microhardness, thermal resistance, impact resistance.

Introduction. Currently, thin sheet glass is used for glazing greenhouses and facades of buildings, in the manufacture of double-glazed windows, solar panels, decorative stained glass, protective and laminated safety glass [1]. Production of flat thin nominals glass is urgent both in terms of reduction of specific consumption material and weight loss of products based on them.

The main methods of producing thin nominal glass are float-method and the method of vertical drawing. However, the float-process has a limit to the minimum thickness of the molded glass (not less than 1 mm) and requires a complex, expensive equipment. Moreover, when moving to thinnominals the productivity of above mentioned molding method reduces and the quality of the glass surface impairs.

Of particular interest in the manufacture of sheet thin nominals glass is a vertical drawing down method [2–6]. Leading manufacturers of flat glass “Corning Glass Works”, “Asahi Glass” and “PPG Inds. Inc.” pay it much attention, being the patent holders of most inventions by this method.

It should be noted that the enterprises of the Republic of Belarus for the production of flat glass of “Gomelsteklo” (float method) and JSC “Grodno Glassworks” (method of rolling) were not ableto organize the production of flat glass with thickness of less than 2.5 mm due to insufficient knowledge of the process of obtaining thinnominals glasses.

Obtaining thin nominals glasses with thickness of 1–2 mm should be considered in the connection with the continuous possibility of their hardening. The reliability of glass service in products and designs, the exploitation durability in construction, household and technology depend on the solution of this problem.

Glass hardening can be achieved by thermal (air) and chemical quenching. Thermal hardening of glass with 1–2 mm thickness is impossible or ineffective, because it requires high starting temperatures, which in its turn creates difficulties associated with the possibility of glass distortion or damaging the surface. For hardening glass with thickness of less than 2 mm chemical methods and, in particular, ion exchange are used.

Ion exchange method allows to increase the strength of glass in 3–6 times preserving its transparency. Glass hardening during its production is especially effective. In this case there is no need to heat the glass, temperature of treatment can vary widely, and there is no deformation of the glass ribbon. Glass and its products acquire improved chemical strength, heat resistance and surface hardness along with the increase in strength [7–10].

Main part. The aim is to develop physico-chemical and technological foundations of thin sheet nominal glass (less than 2 mm thickness) with improved performance characteristics.

The experimental set up has been made to study the process of forming the sheet glass of thin nominals (Fig. 1).

Molding is carried out by vertical drawing down. The peculiarity of the installation is the possibility to localize the heat flow from the heaters in a small volume of the furnace. Itresults in a temperature gradient of 100–150°C and allows us to make thinner preformed glass with thickness of 3–10 mm up to the thickness of 0.2–2.0 mm.

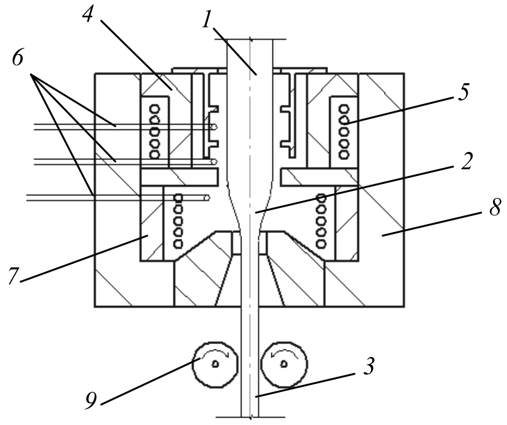

Fig. 1. Apparatus for the study of molding processby vertical drawing down process:
1 – glass ribbon supplied for the molding; *2* – bulb; *3* – moldable glass ribbon; *4* – the top heating furnace unit; *5* – heaters; *6* – thermocouple; *7* – a low heating furnace unit; *8* – refractory lining; *9* – rollers

Parameters of moldable glass ribbon are defined by forming temperature, drawing rate and cooling rate. The minimum value of the transition zone and the stability of the geometric parameters of the glass ribbon are provided by their regulation. The glass is heated in a special construction oven to temperatures of 800–900ºC and stretched into a continuous thin ribbon of glass.

In the process of molding by the inherent flexibility of thin glass, it is moved from a vertical to a horizontal position. The thickness and width of the formable glass ribbon depend on the technological process parameters (viscosity of the glass mass, the glass ribbon speed spinning) and design parameters of the installation (construction of refrigerators, the size of the furnace chamber, and so on).

The sheet float glass with the following chemical composition, %: SiO_2 = 72.8; Al_2O_3 = 1.2; CaO = = 9.7; MgO = 2.7; Na_2O = 13.6 has been selected for the research.

It was found that at glass drawing active molding takes place in the temperature range of 840–850°C, which corresponds to the values of the glass viscosity of 104.8–105 Pa · s. Under these conditions, the astringent effect of the surface tensileforces does not result in a significant narrowing of the glass ribbon. The speed of moldingis within the range of 6–230 m/hr. While molding the glass ribbon at temperatures of 900–950°C (in the active spinning zone) the quality of the glass surface significantly reduces. Raising the temperature in the molding area leads to an increase in temperature in the preparation zone and increases the time of glass presence in the heating furnace with a viscosity of less than 104 Pa · s. It leads to increased astringenteffect of surface tensile forces and significant narrowing of the glass ribbon (under other equal conditions). Moreover, deterioration of the surface of the glass being molded can be caused by the phenomenon of "self-heating". Upon cooling the hot inner layers unevenly heat the thin surface layer (its thickness is not more than 7–10% of the ribbon thickness), which leads to an increase in temperature in the surface layer of the glass due to the heat content of its internal layers. This results in partial melting of the solidified outer layer, and therefore, the process of forming in the transition zone does not stop but continues in the further external cooling of the glass ribbon.

High glass viscosity indicators make molding more difficult in the glass forming temperature range of 800–750°C. On the rollersof drawing device more effort is required butit reduces the efficiency of molding.

The surface quality of glass was studied with the help of a profilometer PROS-130 in order to assess the effect of the technological parameters on the stability of the geometric characteristics of the glass ribbon being molded. The research results are shown in Table 1. The analysis of the surface quality of the samples hasshown that according to the sum of indicators (roughness height, depth of pits and height of the depressions and so on) produced glass is somewhat inferior in quality of float glass.

The height of the roughness, as determined by 10 points for float glass is 0.323 μm, and for (drawn) expanded-glass – 0.38–1.27 μm. The magnitude of this parameter depends on the thickness of the molded glass and increases with the decrease inthe nominal of glass. The ratio of the thickness of the molded glass to a roughness value does not exceed 0.1–0.5%. Thus, the thin nominalsglass in itssurface quality is close to the surface quality of float glass and thus has significantly less weight.

To improve the strength characteristicks of sheet glass of thin nominals we have used the chemical hardening method by low-temperature ion exchange in molten KNO_3.

Table 1

Characteristics of the surface profile of glass samples

Indicators	Indicator value for glass sample					
	Float glass (sample comparison)	1	2	3	4	5
Glass thickness, mm	3.0	0.42	0.27	0.32	0.46	0.36
Forming temperature, °C	–	850	950	900	870	850
Roughness class	12б	11а	9в	11в	12б	11а
Maximum roughness hight R_{max}, µm	0.361	1.27	4.84	0.768	0.588	1.53
The Maximum hight of the roughness Rp, µm	0.207	0.928	4.01	0.476	0.398	1.23
The depth of surface pits R_{vk}, µm	0.107	0.229	0.578	0,225	0.144	0.194
Average step of roughness Sm, µm	6.27	14.6	8.35	7.53	7.28	15.3

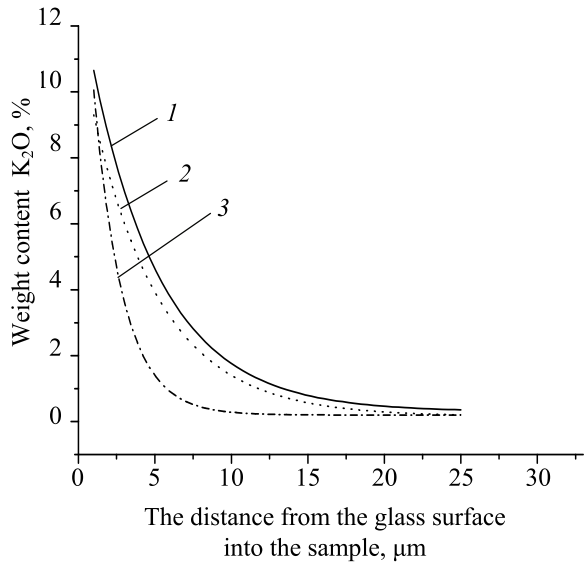

Fig. 2. The Change in the content of K_2O in the surface layer of the glass at its ion exchange hardening for 3.5 hours at a temperature: *1* – 500°C; *2* – 450°C; *3* – 400°C

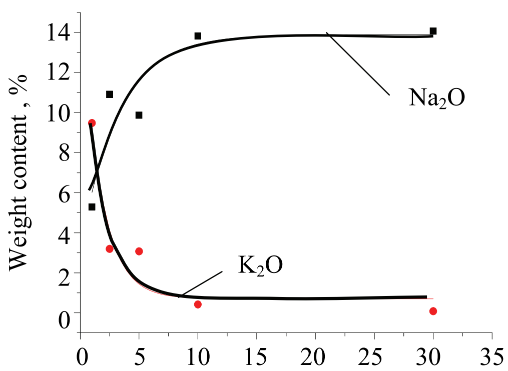

Fig. 3. The change in the content of K_2O and Na_2O in the surface layer of the glass at a temperature of 400°C and the treatment time 3.5 hours

Table 2

Physical chemical properties of the glass before and after chemical toughening

Indicators	Initial glasses	Glass treate data temperature for 3.5 hours		
		400ºC	450ºC	500ºC
Diffusion layer depth, μm	–	10–15		
Thermal resistance, %	180	210	210−220	230−260
Microhardness, MPa	4,800	5,300–5,418	5,300–5,470	5,350–5,710
Symmetrical bending strength, MPa	95	210−220	230−250	280−290
Hardening coefficient at symmetrical bending	–	2.0	2.3	2.8
Hardening coefficient of impact strength	–	2.0	2.3	2.8

Glass was treated at a temperature of 400–500ºC in the melt of KNO_3 for 0.5–3.5 hours. Selection of temperature of IEX-hardening is due to the fact that, on the one hand, its value should provide the resulting KNO_3 melt, on the other hand, the temperature of the melt should not be higher than the glass transition temperature so as not to cause stress relaxation resulting from the diffusion of potassium ions into the surface layer of glass.

The effect of parameters of ion-exchange strengthening on the depth of the diffusion layer and the amount of physical and chemical properties of thin nominalsglass was studied.

The microstructure and chemical (elemental and oxide) composition of the samples was investigated with a scanning electron microscope JEOLJSM-5610 LV with a system of chemical analysis EDXJED-2201 JEOL (Japan).

The depth of diffusion of potassium ions into the surface layer of glassis shown in Fig. 2, 3.

It was revealed that the processing of glass by KNO_3 melt showed a sharp gradient stresses in the depth of the compressed layer. Regardless of the regimes of the processing the nature of K+ concentration dependence is exponential. The diffusion of K+ ions is carried out in the narrow surface-layer of glass the depth of which does not exceed 10–15 μm.

Increasing the time and temperature of treatment causes a significant increase in the concentration of potassium ions in the result of the exchange of Na ↔ K at a depth of not more than 1–2.5 μm, that, presumably, is due to the structural pack of the surface layer and decrease in diffusion coefficient.

The maximum concentration of ion K+, equal to 10.6% is achieved in the surface layer of the glass at a temperature of 500°C and treatment time of 3.5 hours, which gives rise to high values of compressive stress and, as a consequence, increase in the mechanical strength of the glass in 2–3 times and heat resistance of 1.5 times compared tothe original. Comparative evaluation of the physico-chemical properties of the glass before and after ion exchange of chemical strengthening is shown in Table 2.

Analysis of the data shows that the temperature of the ion exchange treatment in the KNO_3 melt has a significant effect on the properties of thin nominals glass. Its increase up to 500°C and processing time up to 3.5 hours provides a significant increase in heat resistance (260°C), microhardness (5,710 MPa), and the mechanical strength of the glass (hardening coefficient 2.8).

Conclusion. The described vertical molding down method is characterized by relative simplicity of apparatus design, and can be used for thinning the sheet glass obtained by rolling, to a thickness of less than 2 mm. Introduction of vertical drawing method in production does not require significant investment and will allow to organize the production of cover glass and slides, which are currently imported from abroad.

It is possible to significantly improve the physicochemical properties of the thin sheet nominal glasses (0.4–1 mm) by low-temperature ion exchange in molten KNO_3.

Along with the increase in the strength the thinned glass acquire high transparency (by reducing the thickness of the glass), higher heat resistance and surface hardness, which significantly expands the field of their application.

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