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ANALYSIS OF THE BACOR REFRACTORIES AFTER THEIR SERVICE IN GLASS FURNACE

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Abstract. The degree of the baddeleyite-corundum refractories erosion depending on the areas of their location in the glass-making furnace in the float glass production was established. With the use of petrographic analysis the influence of chemical and mineral composition and also temperature and gas environment on corrosion of bacor linings was studied. Due to obtained results the recommendations in relation to the increase of glass-attack resistance of the furnace and its service life length were formulated.

Keywords: float glass, glass-attack resistance, glass furnace, bacor linings, refractory, corrosion.

1. Introduction

Providing optimal operating conditions of glass furnaces during their whole campaign determines the reduction of energy and labour costs and also an increase of melting output.

Construction of the tank furnaces for the float glass production is quite conservative. Over the last 130 years, the Siemens' furnaces don't change and are forward-flow regenerative cross-fired with end-charging of batch and cullet. However, the main indicators of their work have changed quite significantly: unit capacity, specific melting output from melting area of the furnace and the campaign length increased, specific fuel consumption decreased by more than ten times, and the melt utilization rate increased from 0.30–0.40 up to 0.85–0.90 [1].

The primary role to solve these problems is given to the development and implementation of new improved performance refractory materials. The composition, properties and state of the melting furnace refractories, which contact with operation environments (arch, walls, siege block, *etc.*) are very important in providing the high quality of the glass products. Along with refractories disposed in the melting zone, above mentioned products with complex configuration, which are part of the working end, also have a great influence on the quality of the glass. That is why they must also meet the high requirements in the performance characteristics, shape and sizes [2].

The most important of these requirements is a significant corrosion resistance to the glass melt, called glass-attack resistance, characterized by the dissolution rate of the refractory in the glass melt. It depends on many factors including the chemical and mineral composition, structural characteristics of the refractory, the chemical composition and viscosity of the glass melt, its value of surface tension at the interface with the refractory lining, *etc.* [3-5].

During their service the refractory parts are not only subjected to the intensive influence of the glass melt, but also significant thermal and mechanical stresses, resulting in the increase of requirements to their heat resistance and strength [6, 7]. In addition, the refractories, used in the glass-melting, should provide the constantly given parameters of the glass melt and its temperature homogeneity [8]. When refractories interact with the glass melt the contact layer forms, and it is characterized by a significantly higher viscosity in comparison with the produced glass melt one. Under real conditions the glass melt in the glass furnaces is in constant motion, washing-off the products of the glass melt reaction with the refractory.

The aim of the present work is to establish the character of corrosion of the baddeleyite-corundum refractories in the float glass furnace based on the results of petrographic investigations.

2. Experimental

Analysis of baddeleyite-corundum refractories of the tank furnace were made after 5.5 years of its using in the float-glass production (see Table 1 for its chemical composition) at PJSC "Lysychanskii glass factory "Proletary" (workshop № 2). At the same time the technical characteristics, technological regime parameters and specific conditions of the glass furnace working were taken into account.

Table 1

Chemical composition of float glass, wt %

SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Na$_2$O	SO$_3$
71.9	0.9	0.06	8.8	4.05	13.9	0.39
± 0.3	± 0.15	± 0.01	± 0.2	± 0.2	± 0.2	± 0.01
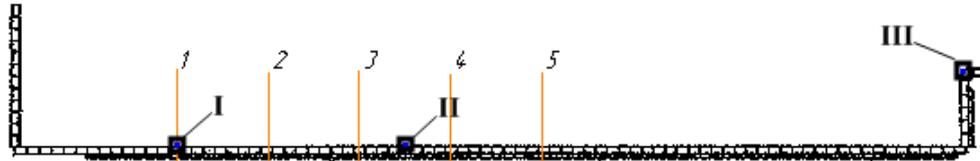
Fig. 1. Scheme of sampling of melting tank lining: axes of the burner portals (1-5); sampling locations (I, II, III)

Table 2

Chemical composition of the investigated bacor refractories

Sample marking	Content of components, wt %				
	ZrO$_2$ (at least)	SiO$_2$ (no more)	Al$_2$O$_3$ (no more)	TiO$_2$/Fe$_2$O$_3$ (no more)	TiO$_2$/Na$_2$O (no more)
AZS-33 (I)	33	15	50.45	0.25	1.3
AZS-36 (II)	37	14	47.35	0.25	1.4
AZS-41 (III)	41	12	45.75	0.25	1

Type of the furnace is regenerative cross-fired, melting capacity is 350 tons of glass melt per day; fuel – natural gas; excess air coefficient $\alpha = 1.02$–1.05 in the zone of the first and second pair of burners; $\alpha = 1.2$–1.6 in the area of 4th pair of burners; specific output of glass melt from 1 m^2 of the heated part of the furnace 1950–2000 kg/m^2; the highest temperatures 1868–1873 K. Wall material of the melting tank – molten-cast baddeleyite refractories: BACOR 33, BACOR 36 and BACOR 41. Suspension wall materials of the melting tank are bacor and Dinas brick, crown – Dinas brick, nozzle of the regenerator – zircon, periclase and chrome magnesite. The intensity of the air blowing of the external walls of the melting tank is 0.9–1.0 m^3/s per 1 m of the wall brickwork [9].

For the investigation the samples of bacor refractories from three different zones of the tank furnace were selected (Fig. 1). Their chemical composition and markings are shown in Table 2. Original sizes of the bacor blocks are (L×W×T) 1220×450×250 mm. The first sample AZS-33 (I) (Fig. 1) was taken from the bath outer stack situated on the axis of the first portal of the burner. The features of the bacor lining's service are: reducing environment flame, the solid-state reactions with the formation of the melt at the border of the gas – melt – batch, intensive convection currents of the glass melt. The temperature of the flame space is 1753 K, the temperature of the glass melt on the bottom of the furnace is 1518 K. At the portal of the first burner an active output and evaporation of the light fractions of the batch take place,

which depositing on the structural elements of the refractory lining, are subjected to the refractory corrosion.

The second sample AZS-36 (II) was chosen between the 3rd and 4th burners in the hotspot zone, corresponding to the highest temperatures in the glass furnace. The erosion of the refractories in that part of the furnace is due to a very low viscosity of the glass melt (10–10^2 Pa·s). Here the convection currents of the glass melt are very strong both the forward and backward (longitudinal) and the transverse ones. Temperature of the gas space is 1868–1873 K, temperature of the glass melt on the bottom of the furnace is 1493 K.

The third sample AZS-41 (III) was taken from the corner block of the glass furnace neck (Fig. 1). Its corrosion is mainly connected with the dynamic load and the multiple powered stream of the glass melt, which washes away the refractory when glass melt comes out from the melting end (width 8400 mm), passes the neck of the glass furnace (width 3700 mm) and comes into the glass elaboration channel. The temperature of the gas space is 1683 K, the temperature of the glass melt on the bottom of the furnace is 1463 K.

Petrographic analysis of the samples were made on the polished sections in the reflected light by NU-2E universal microscope (Carl Zeiss Jena) with 30x–320x magnifications and transmitted polarized light – by MIN-8 microscope using the immersion preparations at 100x–320x magnifications[1].

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[1] Investigations were made by N. Privalova (PhD in geological-mineralogical sciences).

Quantitative ratio of phases in the samples

Sample	Area	Capacity, mm	Content, vol %				
			Baddeleyite	Corundum	Nepheline + glass	Glassy phase	Other phases
AZS-33 (I)	The least changed	> 3	30–35	45–50	–	15–25	
	Working	0.2–1	25–35	1–2	60–70	–	
	Crust	2–7	–	–	–	100	
AZS-36 (II)	The least changed	2.5–3	30–35	45–50	–	15–25	
	Working	0.03–0.1	25–35	25–35	30–50	–	
	Crust	1–2	–	–	–	100	
AZS-41 (III)	The least changed	0.5–1.5	38–40	40–45	–	15–20	Mullite – 3–5
	Working	0.02–0.1	30–35	20–25	30–50	–	Mullite – traces
	Crust	5–15	–	–	–	100	

3. Results and Discussion

The results of petrographic studies have shown that in the samples of baddeleyite-corundum refractories during their service the following areas were formed: the least changed area, working (reaction) area and the area with the crust of glass on the samples surface (Table 3). The least changed area of the AZS-33 (I) sample consists of the tabular, ribbon-shaped, frequently parallel inclusions of the corundum and baddeleyite cocrystallization (solidified eutectic melt) with different lengths and widths, and also contains the glassy phase between the baddeleyite-corundum inclusions.

Baddeleyite is observed in the form of grains (crystals) with isometric (rounded), elongated (oval) and irregular shapes, distributed among the short-prismatic and isometric crystals of corundum. Colourless glassy phase with an index of refraction $N \approx 1.500–1.510$ has also the form of the elongated ribbon-shaped inclusions.

In the glassy phase and inclusions of cocrystallization (in a smaller amount) the pores of the least changed area are isometric and irregularly shaped. Contacts of all phases are dense, only occasionally at the contact "glassy phase – baddeleyite + corundum" the cracks are observed.

Samples AZS-36 (II) and AZS-41 (III) at the least changed area have finer crystallization of both the inclusions of cocrystallization, and the crystals of corundum and baddeleyite in these inclusions themselves, and also glassy phase (Table 4). In the sample AZS-41 (III) the baddeleyite is occasionally observed in the form of separate grains and aggregations, and in the glassy phase at the contact area with corundum the needle crystals of mullite ($3Al_2O_3 \cdot 2SiO_2$) are found, which are up to 0.02–0.04 mm in length.

The sample AZS-36 (II) is indicated with a slightly smaller number of pores and cracks, and in the sample AZS-41 (III) the rounded pores predominate, and their sizes are considerably bigger ones (Table 4).

The structure of the investigated samples is shown in Fig. 2.

In the working (reaction) area of the AZS-33 (I) sample the similar structure is observed. But in the aggregations (inclusions) of cocrystallization only the baddeleyite is kept (Fig. 3), which is freely immersed in the colourless glassy phase with an index of refraction $N \approx 1.510 \pm 0.005$ and with crystallizing in it the prismatic crystals of nepheline (β-$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) and, quite seldom, – of the carnegieite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$), with the length up to 0.03 mm and sometimes subparallel oriented,.

The sample from the working area practically has no pores.

In the samples AZS-36 (II) and AZS-41 (III) the corundum in inclusions of cocrystallization is kept, although in the smaller amount (Table 4), and in its place the glassy phase with nepheline crystals with sizes of 0.004–0.008 mm is marked.

Different capacities crust is observed in the working surface of all samples and represented by the colourless glassy phase with an index of refraction $N \approx 1.520–1.525$, which is close to the float glass index.

Contacts of the working area with the refractory and glassy crust are rough, winding, with penetration of glass in pores and cracks.

Thus, it was found that the glass melt, penetrating through pores and cracks into the refractory, reacts with components of refractory, primarily with glassy phase of bacor and corundum. As a result of this interaction the glass melt is formed similar to the composition of the nepheline according to the index of refraction ($N \approx 1.510$). Also nepheline or carnegieite are crystallised. The gradual substitution of the refractory components for low-melting compounds and slopping and/or washing-off of the intensively changed layer occur.

The results confirm that corrosion of refractories with marks AZS-33, AZS-36, AZS-41, taken from the different areas of the glass furnace, has a similar character, but with some certain features which may be associated with the specific conditions of their service.
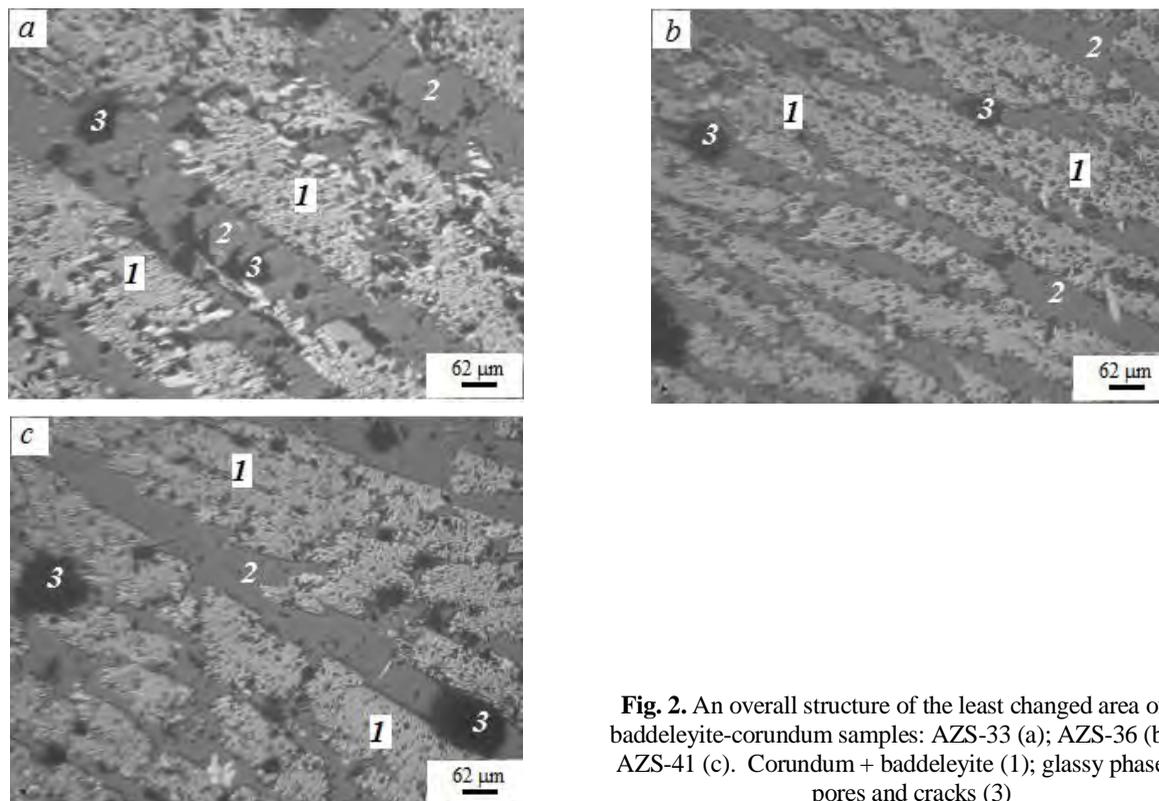
Fig. 2. An overall structure of the least changed area of the baddeleyite-corundum samples: AZS-33 (a); AZS-36 (b) and AZS-41 (c). Corundum + baddeleyite (1); glassy phase (2); pores and cracks (3)

Table 4

Structure characteristic of the baddeleyite-corundum samples of the least changed area

Sample	Prevailing sizes, mm				Width of the glassy phase inclusions, mm	Sizes, mm	
	Aggregations of the cocrystallization		Crystals in the aggregations			Pores	Cracks
	Length	Width	Baddeleyite	Corundum			
AZS-33 (I)	$\dfrac{5-15}{16^*)}$	$\dfrac{0.1-0.5}{0.6}$	$\dfrac{0.007-0.04}{0.06^*)}$	0.004-0.015	$\dfrac{0.02-0.1}{0.2}$	$\dfrac{0.004-0.04}{0.08}$	Up to 0.2-0.4
AZS-36 (II)	$\dfrac{0.5-2}{5^*)}$	$\dfrac{0.05-0.3}{0.5^*)}$	$\dfrac{0.008-0.03}{0.05^*)}$	0.004-0.010	$\dfrac{0.03-0.06}{0.08}$	0.004-0.015	Up to 0.2
AZS-41 (III)	$\dfrac{0.2-2}{5^*)}$	$\dfrac{0.05-0.3}{0.5^*)}$	$\dfrac{0.008-0.03}{0.06^*)}$	0.004-0.010	$\dfrac{0.04-0.06}{0.08}$	$\dfrac{0.05-0.2}{0.3}$	Up to 0.3

Note: * the maximum size in the denominator

Fig. 3. Structure of the working (reaction) area of the baddeleyite-corundum sample AZS-33 (I): corundum (1); baddeleyite (2); glassy phase (3); pores and cracks (4)
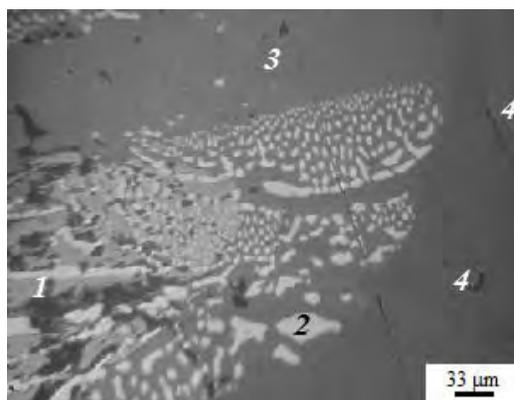
4. Conclusions

On the basis of the obtained results of petrographic investigations of the bacor refractories with marks 33, 36 and 41 after their use in the glass furnace for the float-glass production and taking into account their comparatively long-time working (about 5.5 years), it can be concluded that it is necessary to select and use the refractories of higher quality, which would contain the minimum of the glassy phase. Furthermore, during the constructing of the glass furnace it should be paid attention to reducing of the number of the suture lines and preventing the contacts of the refractories between each other and with the melt as well, because of its ability to give the low-viscosity eutectics. Also the formation of the small cracks during the furnace preparation to the glass melting should be prevented.

References

[1] Popov O., Tokarev V. and Ignatyev S.: Steklo i Keramika, 2008, **3**, 3.

[2] Rossikhina G., Podholyuzin V., Doroganov V. *et al.*: Steklo i Keramika, 2006, **11**, 24.

[3] Le Bourhis E.: Glass: Mechanics and Technology. WILEY-VCH GmbH & Co., Weinheim 2008.

[4] Schaeffer N.: Tekhnolohiya Stekla. CTI-Print, Kishinev 1998.

[5] Guloyan Yu.: Steklo Mira, 2001, **3**, 39.

[6] Yashchishin Yo.: Tekhnologiya Skla, Ch. 2: Osnovy Tekhnologii Sklyanoi Masy. Beskid Bit, Lviv 2004.

[7] Guloyan Yu.: Fiziko-Khimicheskie Osnovy Tekhnologii Stekla. Tranzit-IKS, Vladimir 2008.

[8] Pankova N. and Mikhailenko N.: Teoriya i Praktika Promyshlennogo Steklovareniya. RHTU im. D.I. Mendeleeva, Moskva 2003.

[9] Yaitskiy S., Bragina L. and Yaitskiy N.: Vestn. Nats. Techn. Univ. Kharkiv. Polytech. Inst., 2012, **32**, 72.

АНАЛІЗ СТАНУ БАКОРОВИХ ВОГНЕТРИВІВ ПІСЛЯ ЇХ СЛУЖБИ У СКЛОВАРНІЙ ПЕЧІ

Анотація. Встановлено ступінь руйнування баделеїто-корундових вогнетривів залежно від зон їх розташування у скловарній печі при виробництві флоат-скла. З використанням петрографічного аналізу вивчено вплив хімічного та мінерального складу, а також температури й газового середовища на корозію бакорової футерівки. За отриманими результатами сформульовано рекомендації щодо підвищення склостійкості печі та подовження термінів її служби.

Ключові слова: флоат-скло, склостійкість, скловарна піч, бакорова футерівка, вогнетрив, корозія.