INVESTIGATION ON CORROSION RESISTANCE OF CHROMIC OXIDE, AZS / CR AND HIGH-ALUMINA REFRACTORIES TO ALUMINABORONSILICATE GLASSES AND BASALT MELTS

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ABSTRACT

The corrosion resistance researches of widely used for the lining of glass furnaces refractories to aluminaboronsilicate glasses and basalt melts were carried out. Samples of chromic oxide, sintered AZS with addition 30 % and 60% of Cr_2O_3 and high-alumina refractories were tested during 8 hours by dynamic method for corrosion resistance at 1350 °C to textile E-glass melt, at 1400 °C to light-protective medical glass melt and at 1450 °C to basalt melt. Besides, samples of these refractories were tested during 8 hours by crucible (static) method for corrosion resistance mentioned melt at the same temperatures and at 1580 °C. The features of refractories corrosion character by used glasses and basalt melts tested by both methods were determined. Based on obtained results of researched refractories corrosion resistance recommendations for optimal usage of these refractories in high-load places of glass furnaces lining were composed.

INTRODUCTION

Glass-melting furnaces are complex large-sized continuous units, the working lining of which is under constant long-term corrosive and erosive effects of aggressive glass or basalt melts, charge components, and gas streams at high temperatures. When operating glass-melting furnaces, special attention is paid to increasing their productivity and at the same time extending overhaul campaigns. To solve these problems, progressive methods of glass-making processes control are used, glass compositions are optimized, furnace designs are improved, etc. Such changes impose additional requirements on the quality of the applied refractories and cause necessitate development of new types of refractories for use in various sections of the furnaces from the standpoint of their equal resistance.

The Ukrainian research institute of refractories named after A.S. Berezhnoy is producing high refractory sintered high-alumina, chromic oxide, AZS / Cr with 30 % and 60 % Cr_2O_3 refractories intended for furnaces glass-melting lining [1–10]. Present work is devoted to studies of the corrosion resistance of these refractories to aluminaboronsilicate glasses and basalt melts in order to expand their areas of application [1].

EXPERIMENTAL PART

At presented below researches next refractories were used:

1 - High-alumina (HA) refractories of MKT-89 brand, with high thermal shock resistance, made from coarse fused alumina and mullite with alumina matrix. Widely used as drop-forming units (plungers, bushings, points, etc.), gates, plates and other products at glass-making furnaces of container and medical glass production;

2 - Chromic oxide (Cr_2O_3) refractories of KSU brand, dense, made from fine masses of chromium oxide and titanium dioxide. Widely used for service in contact with the glass E melt as lining of the pool and the feeder of glass-making furnaces of glass E fiber production;

3 – AZS / Cr-30 refractories of KKhTsS-30 brand with 30 % Cr_2O_3, made

from coarse fused alumina with matrix from alumina, zircon and chromium oxide. Widely used in places where the components of the glass E charge and melt are exposed, as lining the topside of glass-making furnaces of glass E fiber production;

4 – AZS / Cr-60 refractories of KKhTsS-60 brand with 60 % Cr_2O_3, made from coarse fused AZS (bacor) and coarse sintered solid solution of TiO_2 in Cr_2O_3 with matrix from alumina and chromic oxide. Widely used as lining elements of topside sections of glass-making furnaces of glass E fiber production in such as zone of bubbling, inlet into the chimney, zone of the recuperator, exposed to the most intense effect of glass E components and gas streams at high temperatures.

The properties of the investigated refractories are given in Table I.

Table I. Properties of used HA, Cr_2O_3, AZS / Cr-30 and AZS / Cr-60 refractories

Properties	Refractories No			
	HA	Cr_2O_3,	AZS / Cr-30	AZS / Cr-60
	1	2	3	4
Mass content, %				
Al_2O_3	81.0	–	61.0	30.0
Cr_2O_3	–	92.4	30.2	57.5
ZrO_2	–	–	5.8	9.1
TiO_2	–	4.1	–	1.2
Apparent Density, g/cm^3	3.2	4.5	3.4	3.5
Open Porosity, %	14	9	22	23
Cold Crushing Strength, N/mm^2	120	>200	85	110

Corrosion resistance tests of refractories by dynamic and static (crucible) methods were carried out in next conditions: to E glass melt (E) - at 1350 °C, to light-protective medical glass melt (M) - at 1400 °C, and to basalt melt (B) - at 1450 °C. Chosen test temperatures correspond to the service temperatures in the production zone of the melting furnaces of the indicated glasses.

Refractory samples were also tested on corrosion resistance by the static method at a higher temperature of 1580 °C, corresponding to the temperature in the melting zone of glass-melting furnaces, in order to create overloaded severe temperature conditions for the experiment. The chemical composition of glasses and basalt is given in Table II.

The dynamic tests of refractories for corrosion resistance were carried out on cylinders samples Ø16mm, L 120mm with a fixing hole. The sample was lowered 50 mm into the depth of a melt, located in a stationary refractory crucible, than sample was rotated in the melt at the test temperature for 3 hours with a constant speed of 17 turn/min. This rotation speed is equal to the linear speed of glass movement along the refractory surface 22×10^{-3} m/sec, which is approximately in 10 times higher than the real maximum speed of glass melt movement in the flow of the glass furnace. At the end of the test, the sample was taken out of the melt. After cooling to room temperature, the nature of its interaction with the glass melt was investigated in the axial section of the sample.

Corrosion resistance tests of refractories by the static method were carried out on samples 40 × 40 × 40 mm, in which a cylindrical hole (Ø18 mm, L 18 mm) was drilled along the vertical axis, and than, filled in with crushed glass or basalt. After that, the samples were heated during 8 hours test temperature. After cooling on the axial section of the samples, the area of erosion and impregnation of the refractory with glass or basalt melts was determined.

Table II. Chemical composition of textile E glass, light-protective medical glass and basalt used for corrosion resistance testing of refractories

	Content, % mass									
	Al_2O_3	SiO_2	B_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	L.O.I.
Textile E glass (E)	14.75	52.5	9.37	0.3	18.6.	3.9	0.14	0.09	0.2	0.2
Light-protective medical glass (M)	6.2	73.8	8.4	0.1	2.6		7.9	0.5	0.3	0.2
Basalt (B)	14.7	51.3	–	14.4	8.86	5.55	1.98	0.84	2.07	0.3

Petrographic studies[1] of the structure and phase composition of the samples after testing were carried out in immersion preparations in transmitted polarized light and on polished sections in reflected light.

RESULTS AND DISCUSSION

Photos of samples axial sections after testing at the same temperatures by the static method, as well as the values of the area of their impregnation and erosion by melts are given in Table III, and at a temperature of 1580 °C - in Table IV.

As shown by the study, the samples after testing for corrosion resistance by the dynamic method did not change their geometric dimensions (Fig. 1). The surface of the samples is covered with a thin layer of glass or basalt. The axial section of most of the samples shows a zone of melts penetration with a depth of 1–2 mm. The lowest penetration is observed in chromic oxide samples with a basalt melt and in high-alumina samples with a light-protective medical glass melt, and the highest in high-alumina samples with a basalt melt.

After tests by the static method at temperatures of 1350, 1400 and 1450 ºC, a residual amount of crystallized glass or basalt melts remained in the wells of all samples (Table III). The walls of the holes did not corrode during the test. All samples have a shallow penetration zone. As well as after testing by the dynamic method, chromic oxide samples with a basalt melt and high-alumina samples with a melt of light-protective medical glass have the lowest penetration, the highest - high-alumina samples with a basalt melt.

After tests by the static method at 1580 ºC, the penetration at all samples with melts increases significantly (Table IV). The residual amount of glass is present only in the samples after testing for corrosion resistance to the melt of light-shielding medical glass. High-alumina samples with basalt and E-glass melts have the largest penetration area (they also show insignificant erosion of the hole walls by these melts), the lowest – in chromic oxide samples. Samples of AZS / Cr-30 refractories are characterized by a larger area of penetration with glass and basalt melts compared to specimens of AZS / Cr-60 refractories.

As a result of carried out studies of high-alumina, chromic oxide, AZS / Cr-30 and AZS / Cr-60 refractories samples after corrosion resistance tests to melts of textile E-glass, light-protective medical glass and basalt, both dynamic and static methods, at various temperatures established, that chromic oxide refractories are the most stable, followed by AZS / Cr-60 and AZS / Cr-30 with 60% and 30% of Cr_2O_3 accordingly. High-alumina refractories are characterized by the lowest penetration by melt of protective medical glass at 1400 ° C and the highest penetration by basalt melt at 1450 °C in comparison with other tested refractories, and also have a similar penetration by textile E-glass melt at 1350 °C.

[1] Carried out by T. G. Tyshyna.

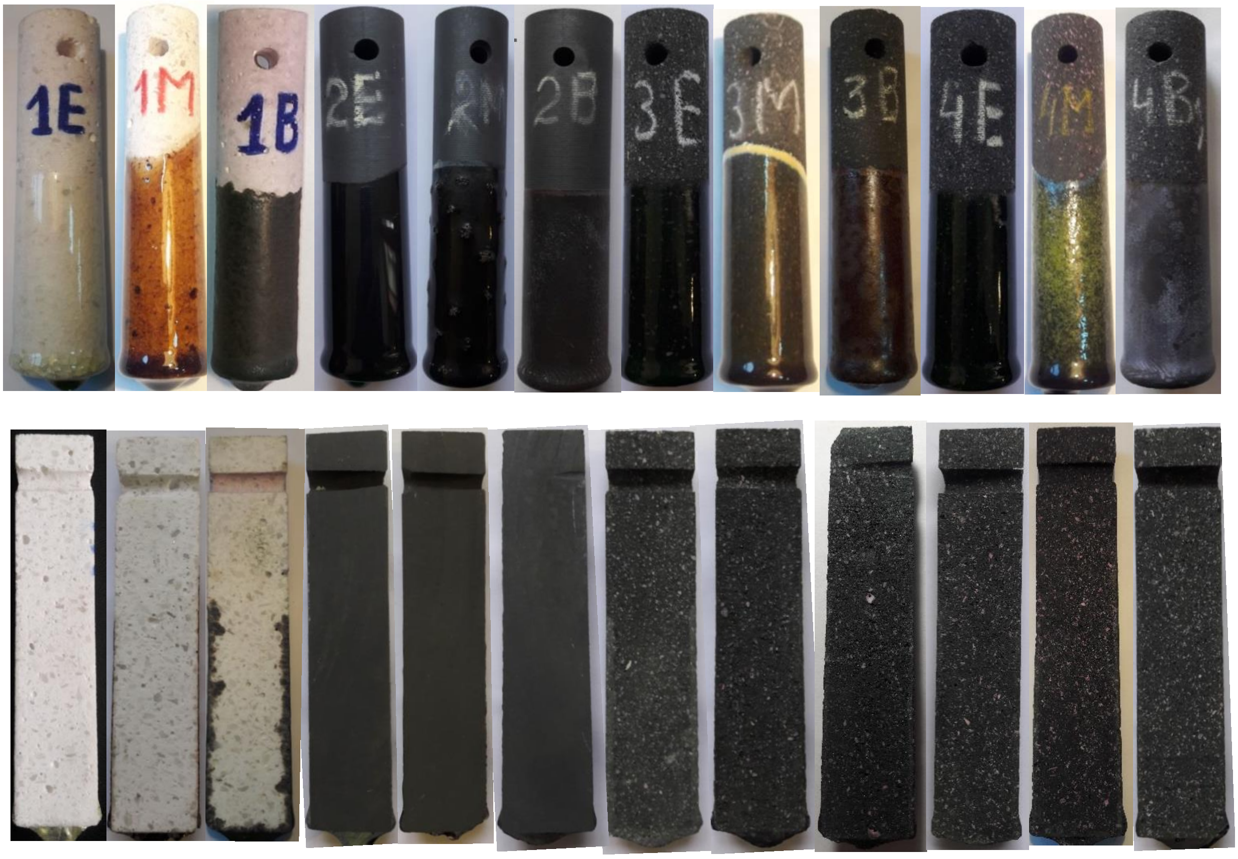


Fig. 1. Photo of samples and their axial sections after dynamic corrosion resistance testing to E, M and B melts of: 1 – HA, 2 – Cr_2O_3, 3 – AZS / Cr-30 and 4 – AZS / Cr-60 refractories.

At 1580 °C, high-alumina refractories have the largest penetration area by these melts influence, and some corrosion of this type of refractories by textile E glass and basalt melt were observed. The most resistant at this temperature to all types of tested melts is chromic oxide refractories. Refractories AZS / Cr with 60% Cr_2O_3 and AZS / Cr with 30% Cr_2O_3 at 1580 ° C are characterized by significant penetration by textile E-glass and light-protective medical glass melts, as well as significant penetration by basalt melt.

The least aggressive in relation to investigated refractories is medical light-shielding glass. At a service temperature of 1400 ºC, high-alumina, chromic oxide, AZS / Cr with 30 % and 60 % of Cr_2O_3 refractories can be used in contact with the melt of this glass. These refractories can also serve in contact with a textile E-glass melt at 1350 ºC. High-alumina refractories cannot be recommended to serve in contact with the basalt melt, while the rest of tested refractories can be recommended to use at 1450 ºC in contact with the basalt melt. At 1580 ºC with the contact of investigated aluminaboron-silicate glasses and basalt melts, it is possible to use only chromium oxide refractories.

CONCLUSIONS

Studies of the corrosion resistance of sintered high-alumina, chromic oxide and AZS / Cr with 30% and 60% Cr_2O_3 refractories to melts of textile E glass at 1350 °C, light-protective medical glass at 1400 °C and at 1450 °C both by dynamic and static methods have been carried out, as well as by the static method at 1580 °C.

Table III - Photos of axial sections of samples, tested at different temperatures by the static method, area of melt penetration or corrosion.

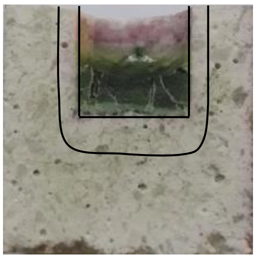
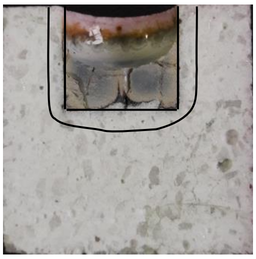
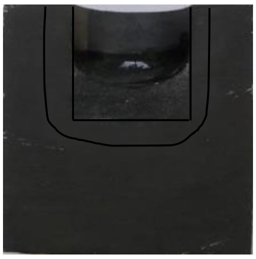
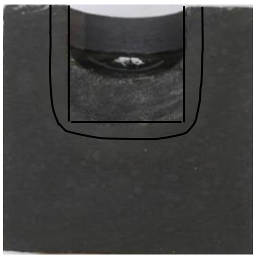
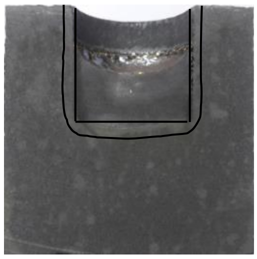
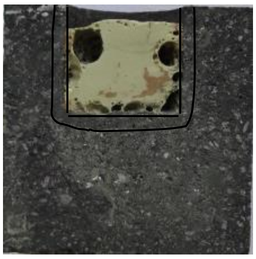
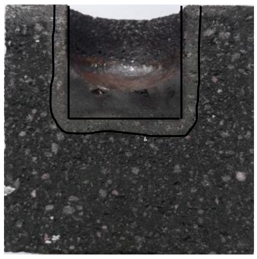
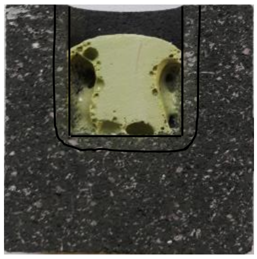
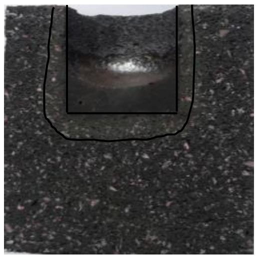
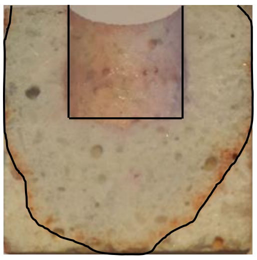
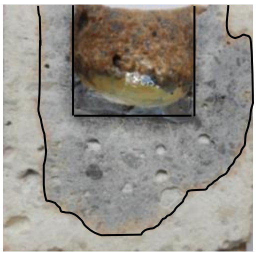
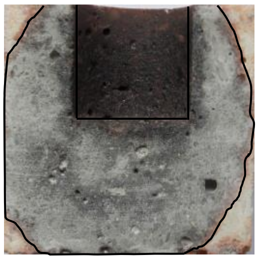
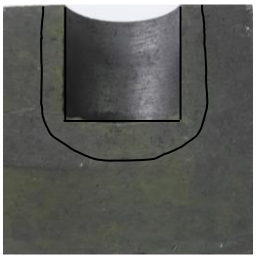
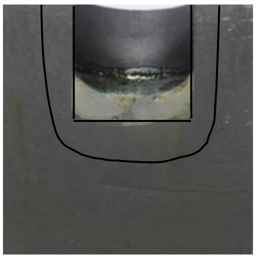
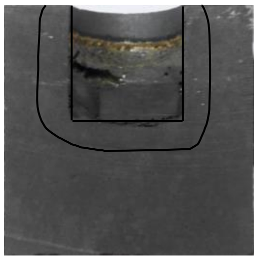
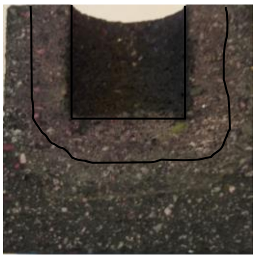
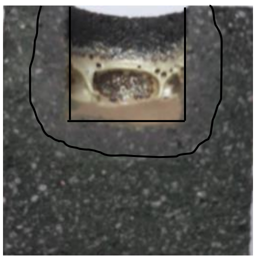
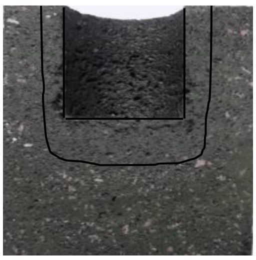
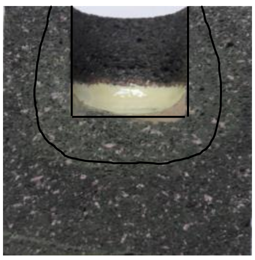
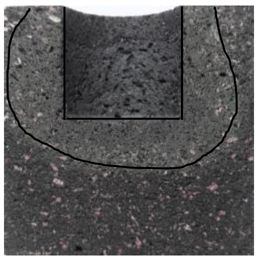
Refractories Name	$\frac{\text{Melt penetration area, mm}^2}{\text{Corrosion area, mm}^2}$					
	E	Sample section	M	Sample section	B	Sample section
HA	$\frac{125}{0}$	 1350 °C	$\frac{85}{0}$	 1400 °C	$\frac{170}{0}$	 1450 °C
Cr_2O_3	$\frac{108}{0}$	 1350 °C	$\frac{95}{0}$	 1400 °C	$\frac{80}{0}$	 1450 °C
AZS / Cr-30$_3$	$\frac{122}{0}$	 1350 °C	$\frac{105}{0}$	 1400 °C	$\frac{150}{0}$	 1450 °C
AZS / Cr-60	$\frac{113}{0}$	 1350 °C	$\frac{100}{0}$	 1400 °C	$\frac{135}{0}$	 1450 °C

Table IV - Photos of axial sections of samples, tested at 1580 °C by the static method, area of melt penetration or corrosion.

Refractories Name	Melt penetration area, mm^2 / Corrosion area, mm^2					
	E	Sample section	M	Sample section	B	Sample section
HA	1022 / 20		651 / 0		1056 / 10	
Cr_2O_3	266 / 0		245 / 0		238 / 0	
AZS / Cr-30$_3$	310 / 0		295 / 0		531 / 0	
AZS / Cr-60	279 / 0		273 / 0		418 / 0	

On the basis of obtained corrosion resistance test results of investigated refractories, recommendations were composed for optimal use of these refractories in glass furnace linings in directed or possible contact with melts of textile E-glass, light-protective medical glass and basalt at different temperatures

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