Study of aluminosilicate refractories after operation in the presence of fluorine-containing wastes

***E. A. Sidorina**, Doctoral Candidate[1], e-mail: elena.sidorina.78@mail.ru;*
***A. Z. Isagulov**, Dr. Eng., Prof., Executive Director[1];*
***I. D. Kashcheev**, Dr. Eng., Prof., Dept. of Chemical Technology of Ceramics and Refractories, Institute of New Metallurgical Technologies[2];*
***K. G. Zemlyanoy**, Cand. Eng., Associate Prof., Dept. of Chemical Technology of Ceramics and Refractories, Institute of New Metallurgical Technologies[2], e-mail: kir77766617@yandex.ru*

[1] Karaganda Technical University named after Abylkas Saginov, Karaganda, Republic of Kazakhstan
[2] Ural Federal University, Ekaterinburg, Russian Federation

Samples of aluminosilicate refractory after operation in the shaft and in the hearth of a coke-gas cupola were investigated; this cupola was used for smelting of cast iron with spheroidal graphite using carbon wastes from aluminium electrolysis production as a reducing agent. Use of only fluorine-containing carbon wastes as a solid fuel in cast iron production allows to utilize hazardous man-caused wastes, improves the economic performance of production and has influence on resistance of fireclay refractories.
It was established that the products acquire a distinct zone features during the service, due to penetration of the components of gas and liquid phases and the effect of low-boiling components of carbon-containing wastes. Upon that, changes in the structure along the distance from the working space are complex ones in lining thickness and in concentration of volatile components in the “cold” parts of the lining.
Permanent character of the mullite content in different zones of fireclay products can be traced, as well as a slight increase in the less altered zone, despite the different service conditions. Absence of alkaline and fluoride phases in the zones of refractory products in the pores and structure of the fireclay refractory was established, due to migration of these gaseous phases into the working space of the cupola with their subsequent removal with furnace gases. Additional development of mullite in certain zones of refractory was revealed, resulting by its synthesis from alumina that did not react during fireclay refractories manufacture under the mineralizing action of a fluorine compound.
Use of fluorine-containing carbonaceous wastes as a solid fuel in cast iron production makes it possible to utilize hazardous man-caused wastes, improves the economic performance of production and has slight effect on resistance of aluminosilicate refractories in the conditions of a coke-gas cupola.
Key words: cupola, nodular cast iron, fireclay, fluorine-containing carbon wastes, refractory properties, utilization of hazardous wastes, porosity, apparent density, refractory microstructure, glass phase, mullite, secondary phases
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Introduction

Decrease of production cost is the important factor of competitiveness rising in metallurgy and machine-building; it can be reached both due to increase of interrepair cycle of heat energy reactors as well as to involvement of non-conventional and more cheap raw materials and power resources in production processes. It correlates with industrial processing of man-caused wastes, which allows to combine lowering of man-caused load on the environment and decrease of production cost. The cupola production technology of high-strength cast iron with nodular graphite is considered as one of the examples of production facilities allowing to utilize the wastes with high economical efficiency. This cast iron creates serious competition not only to steel, but also to substantially more expensive alloys on the base of aluminium, magnesium and titanium [1-3].

The coke-gas cupola is the main cast iron production reactor, up to 40 % of all liquid cast iron is melted using this equipment. It is characterized by construction simplicity [4], simple methods to provide the preset specific liquid metal productivity (up to 100-150 t/(m^3·day), easy management on heat and gas dynamic technological procedures, low level of operation expenses, weak dependence of technical and economical parameters on kinds of initial raw material, lowered volumes of harmful emissions.

Duration of the cupola campaign, as well as quality of molten metal are determined by lining resistance in the hard operation conditions. It is subjected to the effect of high temperatures (up to 1600 °C), to chemical corrosion and erosion caused by metallurgical melts and furnace atmosphere, to wear and strikes from charge materials. Refractories which interact with cupola melts, also should not change composition of cupola slag and cast iron. At present time, lining from aluminosilicate refractories is widely used for cupola manufacture, owing to its well price / quality correlation.

Cast iron melting in a cupola is realized using the power of combustion of gas and carbon-containing charge component, which simultaneously forms the conditions

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for drainage and collection of obtained melts, provides uniform gas distribution in the reactor cross section, creates reducing medium in the shaft and participates in cast iron forming. Coke or anthracite are conventionally used as the carbon-containing component [4]. At present time the coke cost and the cost of coking coals are varied within the range 500-514 USD/t [5] and 200-250 USD/t [6] respectively. Replacement of all coke by more cheap fuel allows to improve technical and economical operating parameters of cupolas.

Widening of secondary raw material use, including carbon-containing raw material, is an important efficiency factor of the metallurgical industry in general [7, 8]. Carbonaceous wastes of aluminium electrolyzers can be among such carbon-containing materials. Up to 1,500 t of carbonaceous lining wastes and up to 25,000 t of cinders of baked anodes from aluminium electrolyzers, with minimal carbon content 85 % (mass.), are annually forming only in Russia and Kazakhstan [9]. These wastes are contaminated by harmful substances from cryolite-alumina melt: alkali cations (Na^+, K^+) and fluorine, what does not allow their storing on slime fields. Use of these wastes as a fuel in the metallurgical industry instead of coke, while fluorine and alkali salts will help to fluidize metallurgical slag, is the most simple and efficient method of their utilization [10-12].

The present work investigated the destruction mechanism of refractory lining in the coke-has cupola during nodular cast iron production; carbon-containing wastes of the aluminium industry were only used as a fuel. The obtained results will be the base for development of composition and manufacturing technology of refractories with increased resistance in the conditions of alkali- and fluorine-containing furnace atmosphere. It will allow to provide increase of interrepair operation period from 3-5 to 15-30 days and to decrease production cost of nodular cast iron in the coke-gas cupola by 5-7 %.

Materials and methods

The averaged chemical composition of fluorine-containing carbon wastes is presented in the **Table 1**; it testifies that forming of low-melting compounds from charge material and lining will be the main destructive factor for cupola lining.

Table 1. **Chemical composition of aluminium production electrodes wastes**

Components	C	NaF	Al_2O_3	Na_3AlF_6	Na_2CO_3	CaF_2	SiO_2
Content, % (mass.)	62.0	12.0	3.0	13.0	3.5	3.0	3.0

Fireclay refractory of ShB grade from the shaft zone (above tuyeres) and from the hearth zone was examined in this work before and after its service life within one campaign, in the conditions of the coke-has cupola during nodular cast iron production.

Chemical composition of the investigated materials was determined by X-ray fluorescent method using ARL QUANT'X spectrometer manufactured by «Thermo Scientific» company (USA) and the software UniQUANT (Rh K_α-emission).

Variation of the phase composition and melting temperature for the samples was determined via thermographic method at the differential scanning diversion sensor STA 449 F3 Jupiter (Netzsch-Geratebau GmbH) using the software package Proteus Analysis 5.2 according to the technique DIN 51004:1994 "Determination of melting temperatures of crystalline materials using differential thermal analysis".

The phase composition was determined by X-ray phase analysis at the diffractometer Miniflrex 600 (CuK_α-radiation) with rotating anode, fabricated by «Rigaku – Carl Zeiss» company (Japan), equipped with the programs for data management and collection MiniFlex guidance and the package for data processing PDXL Basic. Diffraction maximal values were identified using JSPDS data bank. Semi-quantitative assessment of phases content was conducted using corundum number RIR (Reference Intensity Ratio) according to the Chung method [13].

Apparent density, open porosity and water absorption (by kerosene) was determined according to the GOST 2409-2014 "Refractories. The method for determination of apparent density, open and general porosity and water absorption".

Microscopic examinations and determination of chemical composition of separate structural elements were conducted using scanning electron microscope JEOL JSM 6390LA (Jeol; Japan) with tungsten cathode and registration system for characteristic X-ray emission (capture conditions were 20 кV, SEI, BES, operating state 11 mm), as well as in reflected light with MIM-8 and MIN-8 microscopes.

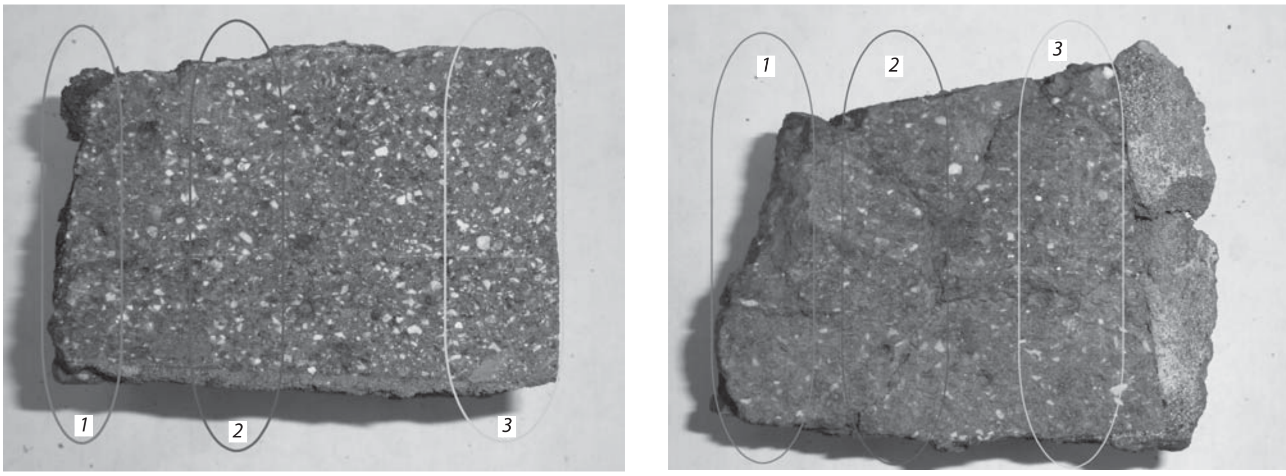
Obtained results and discussion

Products after their service life in the shaft (**Fig. 1**, *a*) are carbonized through whole depth, only molten edge remains on the working surface. Products' geometry on their non-operating planes is practically saved, operating edge was worn uniformly. The melt presents also on the side surfaces of products, what means penetration of the melt or gas phase components into the seams between products. Mechanical destruction of the sample was not observed.

Products after their service life in the hearth (**Fig. 1**, *b*) are characterized by irregular geometry, especially on the working surface, where molten crust with thickness up to 5 mm presents. The samples are sheared with internal cracks originated due to mechanical effect. Molten sections and condensed areas are observed inside products and along the seams with adjacent products. Physical-chemical properties of fireclay samples after their service life in the product's areas are presented in the **Table 2**.

Table 2 data testify:

1. Products acquire zonal structural features after service life in the cupola, at the same time structural variations concerning distance from the working space are complicated in lining thickness (temperature gradient) and in concentration of volatile components in the "cold" part of lining.



a *b*

Fig. 1. Fireclay refractory (cross section) after its service life in the shaft (*a*) and in the hearth (*b*) of the cupola;
1 – operating area; *2* – impregnated (varied) area; *3* – less varied area

Table 2. **Physical-chemical properties of the examined samples**

Sample	Open porosity, %	Water consumption, %	Apparent density, g/cm^3
Product before service life (samples No. 1)	22.0	10.2	2.23
After service life in the shaft (samples No. 3)			
Working area crust (molten)	11.0	4.6	2.43
Working area	13.5	6.0	2.25
Transition area	16.0	8.1	2.23
Impregnated (less varied) area	11.0	7.0	2.29
After service life in the hearth (samples No. 2)			
Working area crust (molten)	14.5	6.2	2.35
Working area	16.5	7.6	2.34
Transition area	19.8	10.0	2.25
Impregnated (less varied) area	17.0	8.6	2.26

Table 3. **Chemical composition of the examined samples**

Samples	Content, % (mass.)								
	Al_2O_3	SiO_2	Fe_2O_3	R_2O	CaO	MgO	TiO_2	S	MnO
Product before service life	37.7	54.3	3.75	0.71	0.58	0.27	1.59	0.008	0.024
Cupola melting slag	18.16	50.26	12.93	0.091	10.18	1.03	1.28	0.15	2.218
After service life in the shaft									
Working area crust	26.4	61.6	5.34	0.21	1.95	0.20	1.52	0.35	0.154
Working area	29.61	57.12	4.22	0.66	1.04	0.29	1.85	0.19	0.126
Transition area	35.25	51.72	3.96	0.71	0.54	0.31	2.16	0.16	0.068
Impregnated area	38.62	50.44	3.12	1.19	0.27	0.47	2.27	0.14	0.016
After service life in the hearth									
Working area crust	3.45	67.27	11.08	0.69	13.17	1.21	2.23	0.15	0.721
Working area	37.36	52.49	4.79	0.80	0.43	0.31	1.94	0.06	0.041
Transition area	25.11	65.92	4.72	1.20	0.49	0.40	1.44	0.29	0.036
Impregnated area	37.22	51.81	3.34	0.86	0.31	0.36	1.95	0.02	0.03

2. After service life in the cupola shaft, products are characterized by more dense structure than after service life in the hearth; it is explained by the effect of volatile charge components (such as fluorides, alkalis). This conclusion is confirmed by more homogenous structure of refractory beyond molten crust in the working area, what testifies about uniformity of the effect of sintering factors on whole refractory structure through lining thickness.

3. After service life in the cupola hearth, products are characterized by more distinct molten crust in the working

area, which was forming during its contact with cast iron melt. They also include the working area which was forming after refractory impregnation of cast iron melt and/or slag, as well as essentially less varied transition and impregnated (slightly varied) areas. Their structure is almost the same as initial refractory structure, though the sintering factor (which operates in the furnace shaft) has the effect on structure density also in hearth lining.

Chemical compositions of the examined samples before and after operation, as well as cupola slag chemical composition are presented in the **Table 3**. Its data testify:

1. Melting of nodular cast iron in the cupola finalizes in manufacture of rather acidic slag (basicity module 0.13), what stipulates necessity of high overheating temperature to provide its fluidity during pouring. Lo content of alkali oxides (0.091 % (mass.)) should be mentioned despite their high content in carbonaceous part of charge material; it means that alkalis and fluorine are evaporating during melting.

2. Zonal chemical compositions of fireclay refractories in the shaft and in the hearth after their service life are close and contain large amount of SiO_2 in the working area, which corresponds to its content in slag. In general, refractory behaviour is mainly described by content of Al_2O_3, SiO_2 and Fe_2O_3 components meeting the requirements of the phase equilibrium diagram $Al_2O_3 - SiO_2 - Fe_2O_3$ within the temperature range corresponding to metal (cast iron) melting.

The samples of fireclay refractory are black after service life in the cupola hearth and shaft, due to saturation of product structure be Fe oxides and soot carbon; its extraction occurs according to the Bel reaction $2CO \leftrightarrow CO_2 + C$. Extraction of soot carbon takes place within the volume of fireclay refractory with porosity equals to 22 % and is accelerated by catalysts (Fe oxides) [14].

Phase composition of initial fireclay refractory and cupola slag is presented in the **Table 4**. It can be seen that mullite and cristobalite (quartzite) are the mineral base of this refractory, with moderate content of glass phase of anorthite composition. Small amount of corundum testifies on use of high-alumina additive in charge material for increase of mullite content in the product matrix.

The cupola melting slag almost completely consists of the glass phase with iron-aluminate-silica composition (fayalite + almandine + anorthite).

Zonal phase composition of fireclay product after service life in the cupola shaft and hearth is presented in the **Table 5**.

The presented data display that glass phase amount in refractory increases up to 30-35 % during operation and its composition varies from mainly anorthite to anorthite-fayalite. At the same time content of Fe oxides (presented as calcium ferrites and iron silicates) in refractory increases and content of refractory phases (mullite and cristobalite) decreases, even taking into account secondary crystallization of mullite during refractory operation. Total content of interstitial phases makes from 9.0 % in the working area crust to 2.8 % in the impregnated, less varied area.

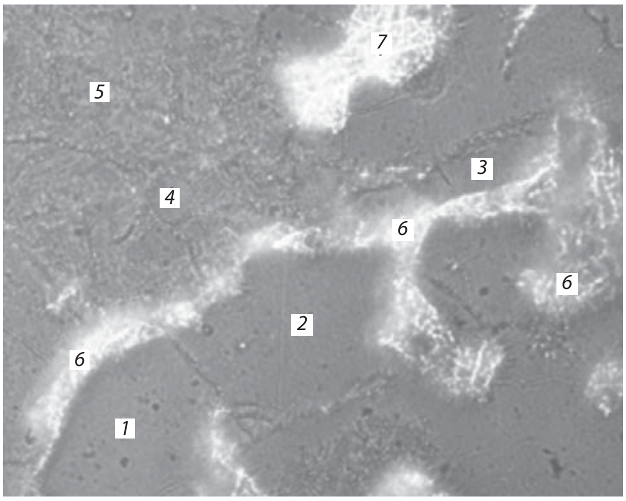
The refractory phase composition varies mainly after service life in the cupola hearth. The refractory working area crust contains practically completely from slag skull: glass phase with ferrite composition (up to 40 %) and wustite (32 %) with residues of refractory phases (mullite 17 % and cristobalite 9 %). Less varied areas also differ by increased content of ferrite phases and substantial lowering of content of primary refractory phases (mullite and cristobalite).

Table 4. **Phase composition of cupola slag and initial fireclay refractory**

Phase title	Formula	Content, % (mass.)	
		Slag	Fireclay refractory
Glass phase	-	70-80	20-25
Corundum	Al_2O_3	-	2-4
Mullite + Iron garnet	$3Al_2O_3 \times 2SiO_2$ $Fe_3Al_2(SiO_4)_3$	-	50-55
Cristobalite	SiO_2	2-4	22-25
Fayalite	$Fe_2(SiO_4)$	5-7	1-2
Wollastonite	$CaSiO_3$	2-5	-
Anorthite	$Ca(Al_2Si_2O_8)$	-	3-5
Magnetite + Wustite	Fe_3O_4 + FeO	2-4	up to 1
Calcium ferrite	$Ca(Fe_2O_4)$+ (Ca, Fe)O	2-6	-

Table 5. **Phase composition of refractory after service life in the cupola shaft**

Phase	Formula	Zonal content, % (mass.)					
		Shaft			Hearth		
		Working area crust	Working area	Impregnated area	Working area crust	Working area	Impregnated area
Glass phase	-	30-35	30-35	25-30	до 40	30-35	25-30
Ranclinite	$Ca_3Si_2O_7$	2.3	0.9	1.0	-	5.1	1.0
Gelenite	$Ca_2(Al_2SiO_7)$	-	1.1	-	-	1.1	traces
Mullite	$3Al_2O_32SiO_2$	38.0	42.0	47.0	17.0	12.0	22.5
Cristobalite	SiO_2	14.0	19.0	19.0	9.0	11.0	12.0
Fayalite	$Fe_2(SiO_4)$	1.7	0.1	0.2	0.7	2,0	2.0
Calcium ferrite	$Ca(Fe_2O_4)$	1.7		2.8	0.2	11.0	traces
Anorthite	$Ca(Al_2Si_2O_8)$	4.0	3.4	-	0.04	12.0	20.0
Wustite	FeO				32.0	0.7	traces
Hematite	Fe_2O_3	1.5	-	-	0.6	2.0	6.0



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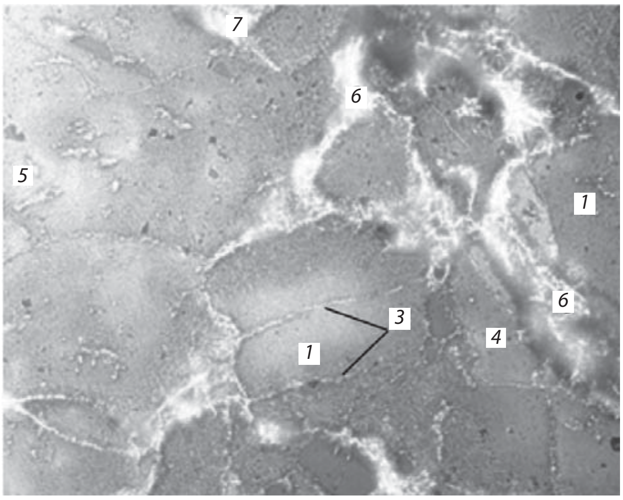

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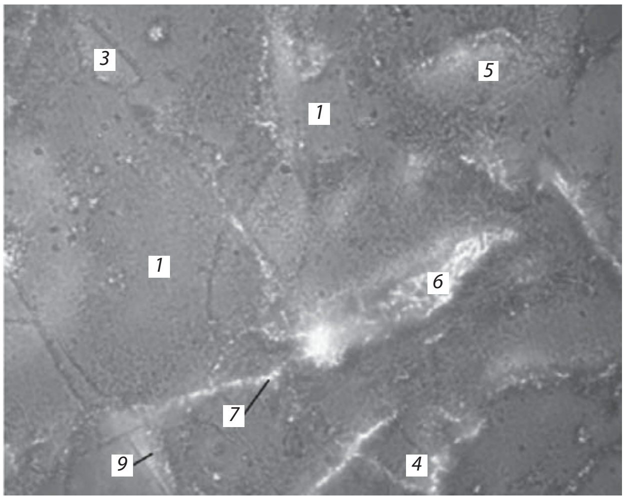

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Fig. 2. Microstructure of the refractory sample after service life in the cupola shaft:
a – working area; *b* – transition area; *c* – slightly varied area; *1* – initial fireclay grain; *2* – primary mullite in fireclay; *3* – primary quartzite; *4* – primary corundum grains; *5* – area impregnated by slag; 6 – iron-silicate glass phase in product's pores; *7* – separate grains of fayalite $FeO \times SiO_2$, hercynite $FeO \times Al_2O_3$ or iron spinel $(Mg,Ca,Fe)O \times Al_2O_3$; *8* – micro-cracks around fireclay grains; *9* – secondary crystobalite around fireclay grains. Reflected light, ×100

Not only physical-chemical properties of fireclay refractories, but also their structure (both on macro- and microlevels vary in the process of operation. Initial macrostructure of products consists of binding crypto-crystalline mass (matrix) and more large fireclay grains, as well as small amount of corundum and cristobalite fine grains (filling agents with different dispersivity), see **Fig. 2**. The matrix of fireclay product is presented by crypto-crystalline binding mass, silicate glass and dispersing fireclay grains, encircled by the finest colourless contours of metastable cristobalite.

The effect of high temperature, reducing atmosphere and CO, which penetrates into the pores, provide dark colour for products and lining. Maximal structural variations are observed in the working areas of products, in the cupola shaft and hearth; these areas are mainly presented by refractories and slag (**Fig. 3**). The working surface of products is covered by slag layer with thickness 2-5 mm and is worn uniformly; in the hearth area, the intensive structural cracking together with slag and metal melts penetration in cracks and pores is observed additionally.

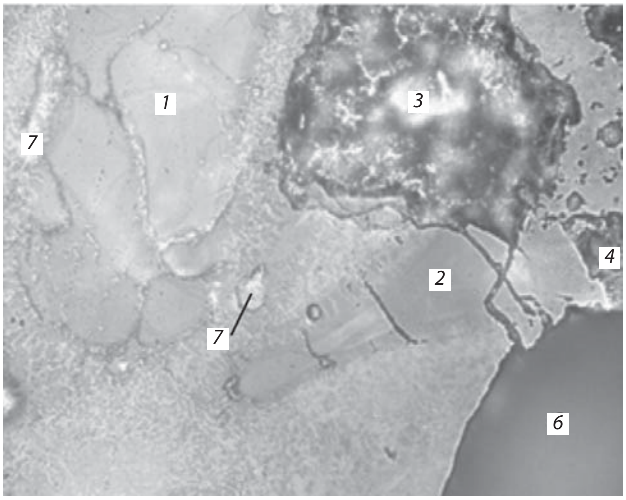
The transition area in products was subjected to smaller structural variations in comparison with the working area. Thereby part of grains was situated on the stage of regeneration and dissolution in glass phase, which contains inclusions with high reflection coefficient (metal or lower metal oxides). Fine-dispersed particles of soot carbon are observed on the surface of grains and glass phase. Pores are characterized by irregular form and are partly (up to 50 %) filled with glass phase.

Slightly varied area of fireclay refractory is more dense after service life in the hearth, it has dark grey colour due to penetration of soot carbon. The refractory structure is not violated, separate fine corundum grains are observed.

Fluorine-containing phases are not reveled in cupola melting slag and in refractories after operation, while abnormal small amount of alkali-containing phases was found out; it means that fluorine and alkali components from carbon wastes of aluminium production with furnace atmosphere in the shaft were mainly eliminated.

The refractory wear mechanisms in the shaft and in the hearth of the cupola are different.

The main effect on refractory in the shaft is provided by gas phase (it includes vapours of alkalis, fluorine compounds which provide enforced sintering) and by reduc-



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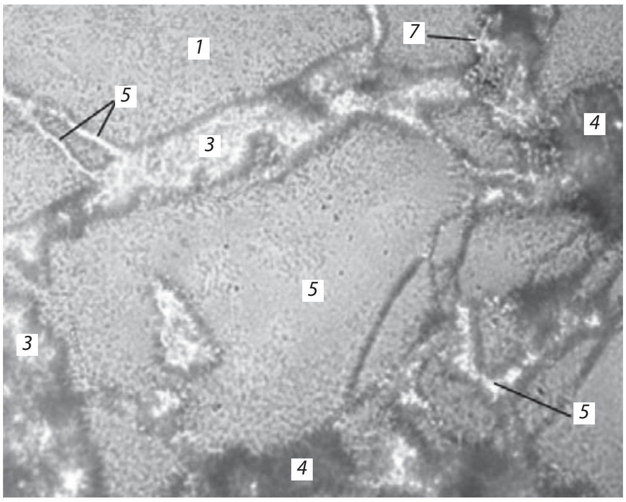

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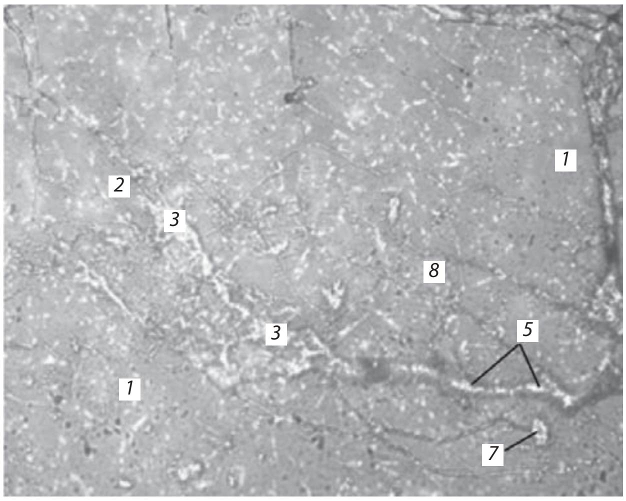

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Fig. 3. Microstructure of the refractory sample after service life in the cupola hearth:
a – working area; *b* – transition area; *c* – impregnated area; *1* – initial fireclay grain; *2* – initial fireclay grain; *3* – iron-silicate glass phase; *4* – area impregnated by slag; *5* – secondary mullite, formed from glass phase; *6* –pore; *7* – separate grains of fayalite $2FeO \times SiO_2$, hercynite $FeO \times Al_2O3$ or iron spinel (Mg,Ca,Fe) $O \times Al_2O_3$ in thin structural pores; 8 – primary corundum grain. Reflected light, ×100

ing atmosphere (leading to forming of soot carbon through the whole volume of lining). Active lower metal oxides and appearing metal phase also effect on the working surface. It leads to intensive chemical wear of fireclay refractory with forming of large amount of iron-containing glass phase with low melting temperature; this glass phase transits in slag melt.

Mechanical loads effect on refractory in the hearth; they exceed the refractory tensile strength for compression. Chemical loads from metal melts and low basic slag also effect on refractory. As a result, refractory in the hearth lining is destructed mechanically and then it is dissolved chemically during the contact of its surface with low basic slag. Iron impregnation by oxides occurs in a glass phase; it is accompanied by iron reduction in refractory volume under the effect of atmosphere.

The features of forming the structure of fireclay refractories in the cupola shaft and hearth are concluded in the following statements.

1. Stability of mullite content in different areas of fireclay products (see table 4) and its slight rise in the impregnated area id distinctly observed.

2. Absence of alkali and fluoride phases in the areas of products due to large partial pressure of the above-mentioned gases (vapours) in pores and structure of refractories is determined, as well as migrations of these phases in the working space with consequent elimination with furnace gases.

3. Additional mullite forming in several zones is stipulated by its synthesis from alumina, which didn't react during manufacture of fireclay refractories; in this case compounds of fluorine and alkalis play the role of mineralizers.

Conclusions

Thereby, the structure of fireclay refractory products after their service life in the cupola shaft, during operation of nodular cast iron melting with use of electrode wastes from electrolysis production as carbon component, is characterized by impregnation by both gas and liquid phases with consequent structure rebuilding. These products are additionally saturated in the hearth by cast iron and slag melt, which effected on refractory and provide its chemical and mechanical wear.

Use of fluorine-containing carbonaceous wastes as solid fuel in cast iron production allows to utilize harmful man-caused wastes, improves economical parameters of production, but has essential effect on the structure of aluminosilicate refractories, destructing at first the refractory matrix. Rise of refractory resistance can be reached due to development of mullite refractories with minimal content of glass phase.

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