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RESEARCH OF CORROSIVE DESTRUCTION MECHANISM
OF CORDIERITE-MULLITE REFRACTORY MATERIALSLviv Polytechnic National University, Lviv, Ukraine
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Abstract. Reasons and mechanism of cordierite-mullite refractory materials destruction in the ovens for glazing ceramic wares baking have been examined. The change of elemental and phase compositions of refractory surface layers under the influence of cyclic action of water vapour and volatile components of glazing coating has been established. The ways of increasing cordierite-mullite refractory materials longevity have been proposed.

Key words: cordierite-mullite refractory materials, high temperature corrosion, thermal stresses, hydrolysis.

1. Introduction

To the present day the main part of ceramic productions uses cordierite-mullite materials as a refractory material in the ovens because they are better by physico-technical and economic values than traditional carborundum materials. But they have insufficient longevity in spite of high thermal and heat resistance and mechanical strength. Under real operational conditions refractory undergoes surface destruction, especially in those cases when baking is carried out in the ovens with insufficient ventilation of the working zone. Destruction and exfoliation of the working surface of cordierite-mullite plates cause ingress of separate particles on the glazing surface of the products leading to the spoilage increase.

2. Experimental

In order to examine the destruction nature of cordierite-mullite refractory materials the complex of physico-chemical investigations has been fulfilled using electron microscopy, infrared spectroscopy, energy dispersion X-ray spectrum microanalysis and X-ray phase analysis before and after exploitation.

3. Results and Discussion

Microstructure of a refractory surface before exploitation is characterized by a high degree of

homogeneity. Pores are uniformly distributed throughout all the material volume; cracks are absent. During refractory exploitation the vitrification of its surface and appearance of separated areas with high micro-heterogeneities are observed already after 90 cycles of baking. The increase of refractory life time till 180 cycles of baking results in a visible damage as the form of exfoliated flakes with 200–350 μm thickness.

The phase composition of cordierite-mullite refractory surface before exploitation (Fig. 1a) is represented by α -cordierite $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ($d/n = 0.408; 0.336; 0.313; 0.303; 0.264; 0.187; 0.167$ nm), mullite $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ($d/n = 0.54; 0.342; 0.254; 0.228; 0.159$ nm) and magnesia-alumina spinel $\text{MgO}\cdot\text{Al}_2\text{O}_3$ ($d/n = 0.468; 0.286; 0.244; 0.202$ nm). At the same time X-ray spectrum of the sample surface is characterized by intensive bands of ^{14}Si , ^{13}Al , ^{12}Mg (Fig. 1), represented in the refractory by the amount of 48.96; 38.23 and 8.02 mas % correspondingly. Moreover, there is an insignificant amount of Na_2O , K_2O , CaO , TiO_2 , FeO (Table).

After 270 cycles of baking there are changes in oxide composition of the sample: the sodium and potassium concentrations increase from 1.38 to 4.97 and 1.04 to 2.18 mas % correspondingly. It is also necessary to note the appearance of plumbum and boron oxides with concentrations of 5.83 and 3.31 mas % correspondingly. At the same time the bands intensity for ^{14}Si , ^{13}Al , ^{12}Mg (Fig. 2) decreases, as well as their oxide concentrations (from 48.96 to 41.98; from 38.23 to 32.76 and from 8.02 to 6.85 mas % correspondingly; see Table).

The character of X-ray spectra shows the absorption of sodium, potassium and plumbum elements by the surface of the cordierite-mullite refractory. These elements are eliminated out of the glazing coating of ceramic wares. The additional saturation of the refractory surface by such oxides causes the formation of alkali-plumbum vitreous phase in the further cycles of baking.

Infrared spectrum of cordierite-mullite refractory before exploitation is characterized by the presence of absorption band at 1200, 1090, 1080 and 900 cm^{-1} typical

Oxide composition of cordierite-mullite refractory

	Oxides content, mas %								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	PbO	B ₂ O ₃
Before exploitation	48.96	38.23	1.25	1.12	8.02	1.04	1.38	0.00	0.00
After exploitation	41.98	32.76	1.07	1.05	6.85	2.18	4.97	5.83	3.31

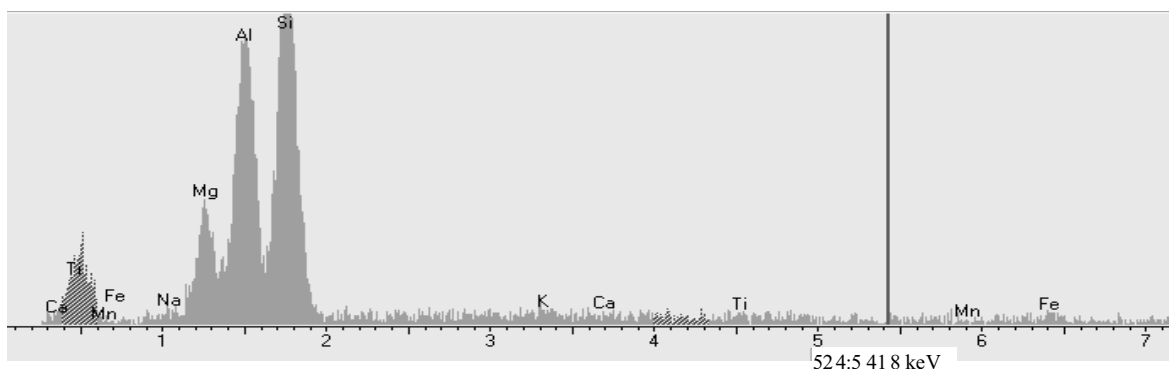


Fig. 1. X-ray spectrum of cordierite-mullite refractory surface before exploitation

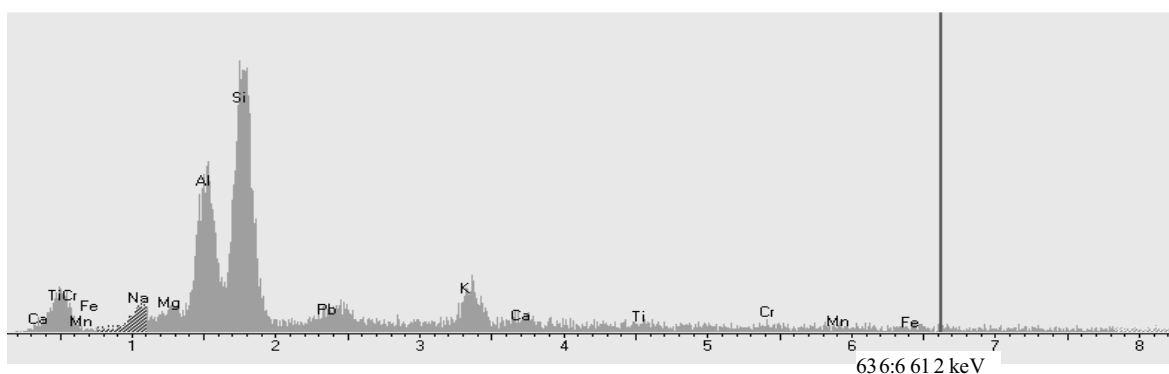


Fig. 2. X-ray spectrum of cordierite-mullite refractory surface after exploitation during 270 cycles of baking

to stretching vibrations of Si–O–Si bonds (Fig. 3a). The absorbance of $[AlO_6]$ -octahedron typical groups should be noted in the area of 690–570 cm^{-1} pertinent to corresponding AlO_6 -chains in the mullite structure (Fig. 3a) [1].

There are also absorption bands in the area of 900–850 cm^{-1} (Fig. 3a) typical for $[AlO_4]$ -tetrahedron, and the maximum at 880 cm^{-1} pertinent to Si–O–Al bond. The characteristic band of the cordierite phase with absorption maximum at 770 cm^{-1} pertinent to $[Si_5AlO_{18}]$ is a peculiarity of refractory IR-spectrum [1]. The location of absorption bands in the area of 485–400 cm^{-1} corresponding to the deformation vibrations of Si–O–Mg bonds and maximums in the area of 365–320 cm^{-1} corresponding to $[MgO_6]$ -octahedron confirm the cordierite presence among refractory phase components. There are no hydrates in the samples before exploitation.

After exploitation the appearance of vibrations at 1640–1580 cm^{-1} (Fig. 3b) indicates the presence of bound water in the cordierite-mullite structure. The maximum at 960 cm^{-1} allows to assume the possibility of aluminum ions hydration in a quadruple coordination with the formation of H–O–Al bonds [1]. The appearance of new maxima in the area of 690–525 cm^{-1} indicates the increase of aluminum ions in the sextuple coordination.

Obviously, the working surface of the cordierite-mullite refractory interacts with water vapours during exploitation in industrial ovens. It is exactly the aluminum cation in the quadruple coordination of the refractory structure that activates the surface with respect to water.

The proceeding of even partial hydrolysis reaction forms active centres over refractory surface. A great amount of water molecules joins to the mentioned active centres at the initial stage of baking. Water bonding results

in additional loosening of material surface and its swelling followed by stresses formation. Destructive action of bound water is intensified under refractory cyclic moistening and desiccation. W. Deer [2] also mentioned the low water resistance of the cordierite phase.

Thus, the destruction of the surface of cordierite-mullite materials is considerably determined by addition of water molecules with the formation of structural Al-OH groups. Monomolecular layer of water bounded with coordination bonds and surface hydroxyls are the matrix over which next layers of absorbed water are formed

owing to hydrogen bonds. The formation of structural hydroxyl groups crushes the surface structure and is accompanied by gradual destruction of cordierite-mullite refractory surface during exploitation.

It is necessary to pay attention to the area of 810–770 cm^{-1} which is characterized by a greater fuzziness and shift to the area of lower values. The reason is a partial deformation of cordierite rings. The fuzzy band in the area of 1200–900 cm^{-1} with slight absorption and duplet formation with the maximum at 1164 cm^{-1} indicates the presence of vitreous phase and crystallization of

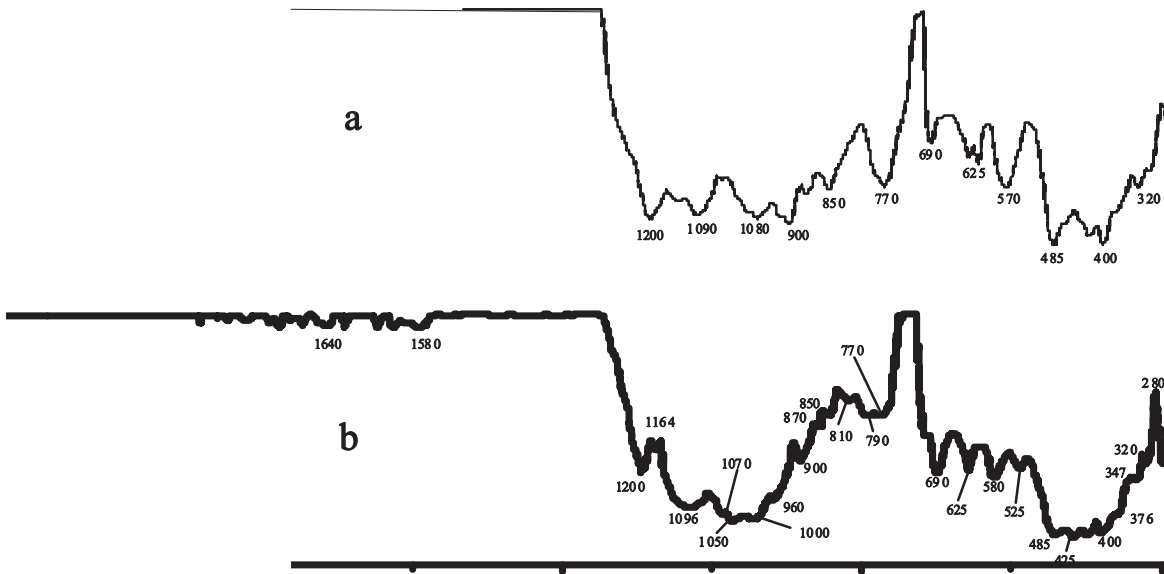


Fig. 3. Infrared spectra of the cordierite-mullite refractory surface before (a) and after 270 cycles of baking (b)

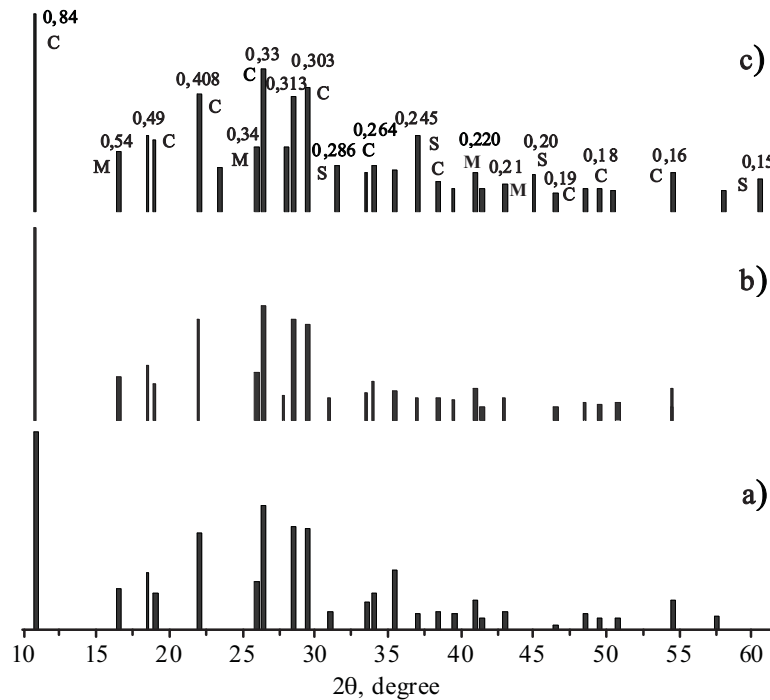
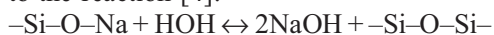


Fig. 4. Dash-rontgenogram of the phase composition of cordierite-mullite surface before (a); after 180 (b) and 270 (c) cycles of baking: C – cordierite, M – mullite, S – spinel

neoformations in $\text{Na}_2\text{O-SiO}_2$, $\text{Na}_2\text{O-PbO-SiO}_2$, PbO-SiO_2 systems [3]. Moreover, the spectrum disorder in the area of $485-400\text{ cm}^{-1}$ (Fig. 3b) indicates the joining of Na^+ , K^+ and Pb^{2+} ions by the surface of cordierite-mullite refractory. This fact may be explained by Si-O-Mg bond possible opening. The introduction of Na^+ , K^+ and Pb^{2+} ions into the material structure at the temperatures of 1193–1323 K establishes initial conditions for eutectic melting at definite microareas resulting further in the increase of the formed vitreous phase amount. The formed alkali-containing vitreous phase is characterized by its ability to interact with water. This fact becomes apparent in hydrolysis accompanied by washing out the alkali metal cations according to the reaction [4]:



The result of interaction between corrosive medium elements and refractory crystal components is the formation of new phases in its surface layers. In order to determine such possibility as well as infrared spectra nature, cordierite-mullite refractory has been analyzed using X-ray phase analysis after exploitation. 180 cycles of baking practically do not change phase composition of refractory surface (Fig. 4b). Dash-rontgenogram of the cordierite-mullite material after 270 cycles of baking shows the intensity increase of magnesia-alumina spinel maxima ($d/n = 0.286; 0.243; 0.238; 0.202; 0.155\text{ nm}$) (Fig. 4c) and fixes the appearance of new diffractive maxima ($d/n = 0.378; 0.318\text{ nm}$). The latter ones may be related to the formation of crystal phases of the following compositions: $\text{Na}_2\text{O-SiO}_2$, $\text{Na}_2\text{O-2SiO}_2$, $\text{Na}_2\text{O-PbO-SiO}_2$ and PbO-SiO_2 which become apparent at IR-spectra in the area of $1100-1080\text{ cm}^{-1}$.

Since the mentioned changes are absent in deep layers of refractory during exploitation we may assume that the formed alkali plumbum-containing vitreous phase in the surface layers intensifies the process of cordierite transformation into magnesia-alumina spinel under the catalytic action of water vapor.

Structural disorder of cordierite phase with further amorphisation of the material form the phases with a high temperature coefficient of linear expansion (TCLE) in surface layers. The increase of vitreous phase content from 11.5 to 42.7 mas % in the surface layer also indicates the structural disorder. The vitreous phase content is determined experimentally by samples treatment in 2% hydrofluoric acid using the procedure described in [5].

The mentioned structural changes during refractory exploitation increase TCLE from $2.3 \cdot 10^{-6}$ to $6.33 \cdot 10^{-6}\text{ K}^{-1}$. The formation of phase with high TCLE under cyclic operation regime of cordierite-mullite refractory materials favors the appearance of stresses in its surface layers followed by cracks formation and material peeling.

4. Conclusions

Insufficient longevity of cordierite-mullite refractory materials during their exploitation in the ovens for glazing ceramic wares baking is concerned with the change of structure and phase composition of refractory surface layers. Under the influence of volatile components of low-temperature glazing the reactive alkali-containing vitreous phase capable to lixiviation is formed. The catalytic action of water vapor at high temperatures in the presence of vitreous phase is a reason for cordierite partial transformation into magnesia-alumina spinel, the thermal coefficient of which is 3 times greater than that of cordierite.

The retardation of the destructive processes may be achieved by applying the coatings of ceramic type on the surface of cordierite-mullite refractory materials. Such coatings have great resistance against water vapor, as well as gaseous sodium, potassium and plumbum oxides. It is necessary to guarantee the low TCLE value choosing the coating type. The coating should be characterized by high compactness, chemical resistance and adhesion to the surface of cordierite-mullite refractory. Also they should possess economic technology of preparing and applying.

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ДОСЛІДЖЕННЯ МЕХАНІЗМУ КОРОЗІЙНОГО РУЙНУВАННЯ КОРДІЕРИТОМУЛІТОВИХ ВОГНЕТРИВКИХ МАТЕРІАЛІВ

Анотація. Розглядається питання виявлення причин та механізму руйнування кордіеритомісних вогнетривів в печах для низькотемпературного випалу полив'яних керамічних виробів. Встановлено зміну елементного і фазового складу поверхневих шарів вогнетривів під впливом циклічної дії водяної пари та летких компонентів полив'яного покриття. Запропоновано напрямки підвищення довговічності кордіеритомулітових елементів печей.

Ключові слова: кордіеритомулітові вогнетривкі матеріали, високотемпературна корозія, термічні напруги, гідроліз.