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PRINCIPLES OF ENSURING THERMAL STABILITY IN INNOVATIVE TECHNOLOGY OF PERICLASE-SPINEL REFRACTORIES

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This article presents the results of research on the structural-phase regularities and behavior of periclase-spinel refractories under high-gradient thermal loads. The findings from the analysis of structural-phase variability in the refractory samples are used to achieve the desired thermal resistance. Based on the investigation of the subsolidus structure of the $MgO-FeO-Al_2O_3-TiO_2$ system, predictions were made regarding the characteristics of solid-phase exchange reactions, considering the existence of solid solutions with various types of crystal structures in specific areas of the system. This enabled the application of new principles for ensuring thermal stability in the developed periclase-spinel refractories, specifically through organizing a fragmented, micro-cracked structure by combining solid-phase exchange reactions with the establishment of mobile equilibrium upon reaching stationary-state temperatures. An additional feature is the possibility of phase invertibility of solid spinel solutions, including changes in the type of spinel structure, in particular quandilite. Physicochemical research methods confirmed the enhanced ability of the material to flexibly adapt its phase composition and microstructure to thermal loads. The feasibility of these principles for achieving the structural-phase adaptability of the material to thermal shocks was validated by electron microscopy analysis.

Keywords: periclase-spinel refractories, herzenite, ulvospinel, quandilite, thermal stability.

Introduction

In recent years, there has been a worldwide trend towards the fabrication of industrial products that are eco-friendly or ensure the cleanliness of technological processes. The environmental component of product performance presents significant competitive advantages in the market and brings in a high level of demand for the long term. Portland cement is still one of the most popular building materials and its production is widely used at leading factories for the disposal of significant amounts of various wastes, including those resistant to decomposition, components of explosives and toxic substances. However, the combustion of various wastes in rotary cement kilns saves fuel, but changes the gaseous environment of burning and causes problems in the composition of the clinker. In particular, it becomes possible to accumulate nitrogen compounds with an oxidation state of +3 in the composition of Portland cement, which are taken to building structures and, when decomposed, cause the emission of ammonia into the air in the buildings. This problem and some ways to solve it are discussed in ref. [1].

The problem of accumulation of chromium compounds with an oxidation state of +6 in cement clinker is very important. All Cr(VI) compounds are extremely hazard; they are carcinogens and can cause the development of human cancers. The sources of such compounds in the composition of cement clinker are refractories back from the high-temperature zone of rotary kilns. Therefore, the most logical technological solution to this problem should be the

replacement of chromium-containing refractories with their other types. It is by no means certain that periclase (MgO) should form the basis of alternative refractories due to the poor wettability of the cement clinker melt and the extremely low solubility in it. However, the technical requirements for such refractories and the limited range of periclase-containing refractories face the problem of developing the production of new types of periclase-containing refractories.

The most stringent technical requirements for the refractories developed in our case are connected with their ability to form a slag lining (or simply a skull, coating) with cement clinker components and to have a heat resistance of at least 9−12 thermal cycles «1300⁰C−water». The skull performs important functions of protecting the lining from shock-abrasive loads of the cement clinker components, reduces thermal conductivity and additionally limits the heating of the metal body of the rotary kiln. In this regard, it is not advisable to use magnesite, periclase, periclase lime and periclase forsterite refractories. Moreover, the last two types of refractories get a certain thickness of the skull, but calcium- and silicon-containing components contribute to the formation of low-melting eutectics in contact with the cement clinker melt, and the corrosion destruction is accelerated due to layer-by-layer dissolution and spalls in the form of flakes from the surface of the refractory.

Periclase-spinel refractories based on aluminum-magnesium spinel ($MgAl_2O_4$) do not get wet and interact weakly [2] with the cement clinker melt, but have good thermal stability close to that of replaced periclase-chromite refractories. A set of scull for periclase-chromite refractories ensures the presence of iron compounds with an oxidation state of +2 in their phase composition [3,4]. In the production of these refractories, the source of Fe(II) compounds is often the initial mineral raw material, chromium iron ore, with chromium spinel ($FeCr_2O_4$) as the main component. Chromium oxide (Cr_2O_3), as well as MgO, does not get wet by the cement clinker melt and, obviously, FeO in the composition of chromium spinel enables it to build up a skull. The chemical affinity of FeO to the cement clinker melt is determined by the variability of the oxygen stoichiometry of the main iron-bearing mineral, brownmillerite ($Ca_4Al_2Fe_2O_{10}$). Therefore, it is advisable to introduce FeO into the phase composition of periclase spinel refractories of the MgO−$MgAl_2O_4$ system. However, even before the start of phase formation reactions, FeO is easily oxidized to Fe_2O_3 and does not produce a necessary effect. Leading companies (in Germany and China) use a method of preliminary synthesis in a controlled gas environment of modifying additives, including spinels in their composition: herzenite ($FeAl_2O_4$), pleonast (($Mg,Fe)Al_2O_4$) [2−4]. In addition, unlike periclase-chromite refractories, where a significant amount of FeO can be present in the form of chromium spinel, the FeO content in the developed refractories should be limited due to the existence of solid solutions with MgO, magnesio-wuestite. The melting point of magnesiolustite drops sharply when increasing FeO concentration, which worsens the refractoriness and deformation temperature under load of such materials. Therefore, it is advisable to inhibit the excessive formation of magnesio-wustites, for example, by introducing TiO_2-containing additives [5−7] capable of synthesizing compounds with a spinel-type crystal lattice: ulvospinel ($TiFe_2O_4$) and quandilite ($TiMg_2O_4$). Accordingly, the MgO−FeO−Al_2O_3−TiO_2 system was selected to develop an innovative technology for a new kind of periclase-spinel refractories.

The aim of this work is to elucidate some structural-phase regularities and features of such refractories under conditions of high-gradient temperature range.

The results of the analysis of the structural-phase variability of the refractory samples were used to achieve a desired thermal stability and expand the well-known technological methods for obtaining heat-resistant refractory non-metallic materials.

Theoretical background, methods and materials

The problem of heat resistance of refractories has been important in connection with the development of new production processes and thermal equipment operating at ever higher temperatures and corrosive stresses. The cause of discontinuity and subsequent destruction of the material under thermal loads is believed to be thermal stresses [8]. The occurrence of thermal stresses is due to the non-free expansion of individual elements of the material structure, which leads to differences in the deformations of local areas and, accordingly, the emergence of counteracting forces. For heterophase and polydisperse materials, the development of thermal stresses is complicated due to some factors: existence of anisotropic crystals, spatial misorientation of polycrystals, the number and topological features of the distribution of the glass phase and pores. In addition, differences in heating conditions (convection, conduction (heat transfer), radiation and their combinations), its speed and maximum temperature, as well as cooling features (in air, in water, etc.) are also important.

The theory of temperature field propagation is extremely complex; it is based on phonon-electron

interactions and is not used in computational practice for heterophase materials. To analyze the resistance of materials, various criteria are used that characterize the ability of the initiation and propagation of cracks. Thus, the dependence of the stability criteria on the tensile strength of the material (more often at break or bending) is taken into account, as well as other ratios: Poisson's ratio, which interconnects the coefficients of elasticity (Young's modulus) and shear; temperature coefficient of linear expansion (rarely taking into account its dependence on temperature); thermal conductivity and other properties. Such a criterion-based assessment of thermal stability requires appropriate equipment and tools; it is difficult due to the lack of standard test methods, and calculation results often do not correlate with experimental data, since they do not take into account many processes (nonlinear creep deformations, introduction of gas phase, etc.). For structural ceramics, energy characteristics, based on the division of the energy of crack formation into elastic energy and effective energy of formation of a new surface, are used. The latter is opposite in sign to the elastic energy, counteracts it and is a kind of excess energy sink due to the stress concentration at the crack tip. Therefore, the main contribution to the effective energy is provided by the change in the Gibbs free energy, the energy absorbed by plastic deformations at the tip and during the movement of dislocations in thin layers on the crack edges. In this case, the fracture energy of the material significantly depends on the grain size, the presence of phases with different hardness values, which can be obstacles to the propagation of microcracks, inhibiting their development and relaxing stresses.

Some results of studies on the dependence of the fracture energy of materials on the grain size give important quantitative information for comparing the ability to resist thermal shock of individual phases of the $MgO-FeO-Al_2O_3-TiO_2$ system. In particular, according to ref. [9], the average destruction energy is as follows: 10 ± 5 J/m^2 for MgO with an intragranular porosity of less than 0.5% (dispersion from 8 to 200 μm); 7 J/m^2 for $MgAl_2O_4$ with porosity from 0 to 2% and dispersion from 2 to 100 μm; 7.5 ± 1 J/m^2 for wustite ($Fe_{0.94}O$) with the above characteristics; ~47 J/m^2 for Al_2O_3 with grain size of up to 50 μm with porosity from 0 to 5%; ~20 J/m^2 for Al_2O_3 with an increase in the grain size of more than 100 μm; ~5 J/m^2 for Al_2O_3 (400 μm); from ~20 J/м^2 (5 μm) to 25 J/m^2 (15 μm) for TiO_2 and sharply decreases with a further increase in the grain size; increases from 10 J/m^2 (1.5 μm) to maximum 38 J/m^2 (10 μm) for $MgTi_2O_5$ and gradually decreases to 25 J/ m^2 (80 μm); increases from 2 J/m^2 (1.5 μm) to 10 J/m^2

(5 μm) for Fe_2TiO_5 and gradually decreases to 5 J/m^2 (30 μm); 2 J/m^2 (5 μm) for Al_2TiO_5 and asymptotically decreases to ~0.5 J/m^2 (25 μm). The noted compounds participate in the processes of phase formation of periclase-spinel refractories, but they are subproducts of the reaction interaction, and this fact makes it difficult to unambiguously interpret their role.

The theory of thermal stability is not able to produce reliable predictions for heterophase and polydisperse materials, being developed now, even in combination with the use of complex instrumental methods for determining structure-sensitive properties and calculating various criteria. Therefore, the heat resistance was determined experimentally by the number of cycles with the refractory specimens between heating up to 1300^{0}C and cooling in running water until the first crack appeared. Samples were drilled from bricks of normal size (3 samples from one brick) with a diamond-coated drill bit. The height of the specimens corresponded to the thickness of the brick, the outer diameter was 50 mm, the end surfaces were not ground and the remains of the edge (the result of breakage at the finishing stage of drilling) were not cleaned.

Physical and mechanical properties were determined by standard methods for refractories, harmonized with European norms (EN) and international standards (ISO). X-ray phase analysis was performed on a DRON-3m diffractometer in CuK_α-radiation. Features of the microstructure were examined on chips and on polished sections of refractory samples using a JSM-6390LV scanning electron microscope with an AZtechEnergy energy-dispersive spectrometer for quantitative determination of chemical elements in local areas of samples (detector X-max 50).

The thermodynamic analysis of solid-phase reactions and the determination of volume effects in these reactions, as well as the analysis of the subsolidus structure of individual ternary subsystems and the $MgO-FeO-Al_2O_3-TiO_2$ system under study were performed according to the procedures described elsewhere [10].

When analyzing the subsolidus structure of individual subsystems and the four-component system $MgO-FeO-Al_2O_3-TiO_2$, data on the existence of solid solutions (in particular, [11]), as well as the results of calculations on the thermodynamic stability of phase combinations [12−14] and the characteristics of eutectics [15] were taken into consideration.

Results and discussion

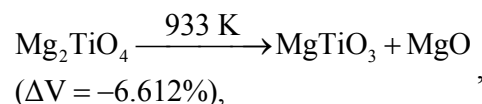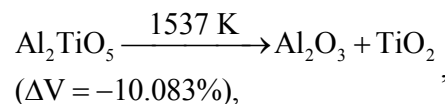The phase composition of the modifying additive was chosen taking into account two following factors:
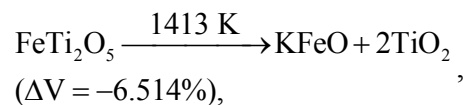
1. The gross (total) oxide composition of the

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additive should belong to the elementary tetrahedron of the $MgO-FeO-Al_2O_3-TiO_2$ system, located far from the concentration area of the elementary tetrahedron $MgO-FeO-MgAl_2O_4-Mg_2TiO_4$, where the calculated bulk composition of periclase-spinel refractory was based.

2. The phase composition of the additive must be polyphasic; it must contain simultaneously individual oxides, their binary compounds, metastable solid solutions, and their decomposition products.

The first factor determines the high thermodynamic probability of solid-phase reaction interaction of the additive phases with the components of the finely dispersed part of the refractory charge during sintering. The second factor determines the multiplicity and branching of the mechanisms of solid-state reactions during sintering due to the change in thermodynamically stable combinations of phases caused by the change of elementary tetrahedra of the system during the path of thermal evolution of each phase of the additive to the final thermodynamically equilibrium phase composition of the material in the elementary tetrahedron $MgO-FeO-MgAl_2O_4-Mg_2TiO_4$. Thus, the maximum number of phases, including middle phases, is involved in the reaction of sintering; moreover, solid solutions delay solid-phase exchange reactions and limit volumetric effects during their course. Moreover, steric phase contacts are developed in the structure of the material, which are most beneficial for the start of solid-phase reactions in the opposite (thermodynamically unfavorable) direction due to it excess energy is absorbed during thermal shock. In this case, the degree of incompleteness of the phase decomposition of solid solutions with crystal lattices (such as pseudobrookite, corundum and spinel), modification transformations

and disproportionation reactions, especially those occurring in the low-temperature range, are of great importance, especially the following reaction:

$$FeTi_2O_5 \xrightarrow{\text{1413 K}} KFeO + 2TiO_2$$
$$(\Delta V = -6.514\%),$$

$$Al_2TiO_5 \xrightarrow{\text{1537 K}} Al_2O_3 + TiO_2$$
$$(\Delta V = -10.083\%),$$

$$Mg_2TiO_4 \xrightarrow{\text{933 K}} MgTiO_3 + MgO$$
$$(\Delta V = -6.612\%),$$

where ΔV is the volume effect of the reaction [10].

The conditions specified above were taken into account when preparing a modifying additive. The phase composition of the additive included (Fig. 1) the following crystalline components (identified values of interplanar distances are indicated in parentheses): α-Al_2O_3 (0.347; 0.255; 0.238; 0.216; 0.208; 0.196; 0.160; 0.140; and 0.137 nm), a solid solution close to the stoichiometry of $FeAlTiO_5$ (0.487; 0.476; 0.339; 0.277; 0.268; 0.234; 0.214; 0.192; 0.181; 0.170; 0.159; 0.156; 0.153; 0.151; 0.146; 0.145; and 0.138 nm); $FeAl_2O_4$ (0.288; 0.245; 0.203; 0.187; 0.156; and 0.144 nm), ulvoshpinel Fe_2TiO_4 (0.301; 0.256; 0.245; 0.212; 0.195; 0.173; 0.165; and 0.150 nm), a solid solution of the complex composition $Al_{0.028}Fe_{2.387}O_4Ti_{0.585}$ (0.255; 0.244; and 0.211 nm), possibly β-TiO_2 (0.623; and 0.300 nm), and FeO (at the background level).
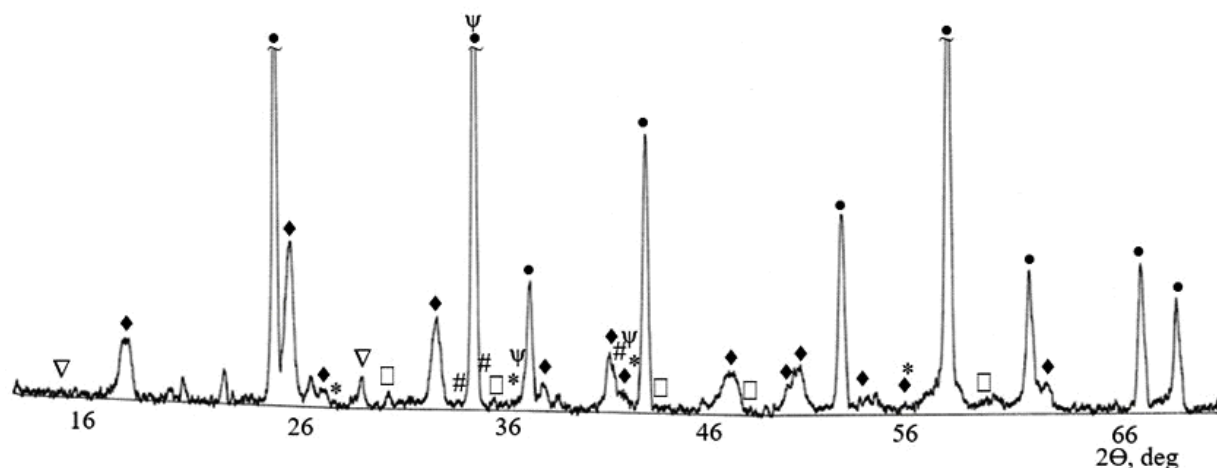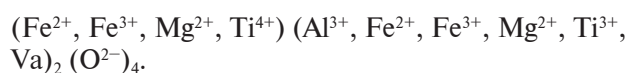

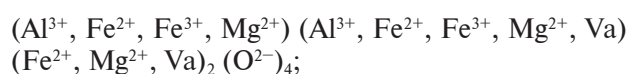Fig. 1. X-ray diffraction pattern of the modifying additive: $\bullet$ – α-Al_2O_3, $\blacklozenge$ – $FeAlTiO_5$, $\square$ – $FeAl_2O_4$, ∇ – β-TiO_2, # – FeO, * – Fe_2TiO_4, ψ – $Al_{0.028}Fe_{2.387}O_4Ti_{0.585}$

The grains of the additive had a water absorption of 6.1%, and the properties of periclase-spinel refractories varied with the introduction of the additive from 2 to 6% within the following limits: apparent density 3.14−3.16 g/cm³; open porosity 16−18%; linear dimensions remained unchanged; compressive strength 39−48 MPa; heat resistance 10−15 thermal cycles «1300⁰C−water». In the microstructure of refractories with 6% modifying additive, large open pores are rare, while small ones (1 μm) are concentrated around large periclase grains, often in the shape of a crescent, which does not prevent direct contact between periclase grains and with the spinel-based matrix phase. Clusters of micropores have the form of foam beds composed of microspheres with different sizes (usually up to 0.4 μm in diameter). This nature of porosity is favorable for maintaining strength and damping deformations under alternating thermal stresses. In the phase composition of this refractory, the following phases are identified (Fig. 2): periclase MgO (0.244; 0.210; and 0.148 nm); monticellite $CaMgSiO_4$ (0.550; 0.415; 0.383; 0.362; 0.316; 0.291; 0.265; 0.257; 0.252; 0.238; 0.221; 0.191; 0.181; 0.174; 0.171; 0.167; 0.159; 0.154; and 0.138 nm); a solid solution with the stoichiometry of the composition $MgFe_{0.2}Al_{1.8}O_4$ (0.469; 0.287; 0.244; 0.202; 0.165; 0.156; and 0.148 nm) and pseudobrookite $FeTi_2O_5$ (0.350; 0.277; 0.246; 0.224; 0.174; 0.161; and 0.137 nm).

In addition, unidentified diffraction maxima are observed on the diffraction pattern, which are either superstructural reflexes during the formation/decomposition of solid solutions or reflexes from the presence of small amounts of structural elements close to forsterite-fayalite solid solutions. The planned phase composition of the refractory is not achieved due to the following reasons: specific firing conditions (insufficient temperature and duration of isothermal holding, oxidizing gaseous environment); the presence of a significant amount of CaO and SiO_2 additives in the original periclase, where the content of additives can reach 14% and cause the synthesis of undesirable phases, in particular, monticellite; and changes in the nature of solid solutions between aluminate and titanate spinels with the $Fe^{2+} \rightarrow Fe^{3+}$ transition, which leads to their decomposition according to the spinodal mechanism with the stabilization of pseudobrookites outside the concentration range of their thermodynamic stability. The latter circumstance is due to the fact that spinel-like phases ($MgAl_2O_4$, Mg_2TiO_4, Fe_2TiO_4 and $Fe_2Al_2O_5$) and continuous wuestite solid solutions MgO−FeO occupy a significant concentration area in the MgO−FeO−Al_2O_3−TiO_2 system and have the same cubic syngony. This fact implies the closeness of structural motifs and the possibility of not only intracationic substitution in certain types of solid solutions with the formation of cationic vacancies (Va), but also cation exchange with each other in significant concentration ranges even with a change in the oxidation state of Ti (+4/+3) and Fe (+3/+2). When comparing the formulas for aluminate and titanate spinels in the most general form, this fact is obvious:

$$(Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}) (Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Va) (Fe^{2+}, Mg^{2+}, Va)_2 (O^{2-})_4;$$

$$(Fe^{2+}, Fe^{3+}, Mg^{2+}, Ti^{4+}) (Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Ti^{3+}, Va)_2 (O^{2-})_4.$$

The polyvariance of the heterovalent cation exchange is a basis for the formation of solid solutions
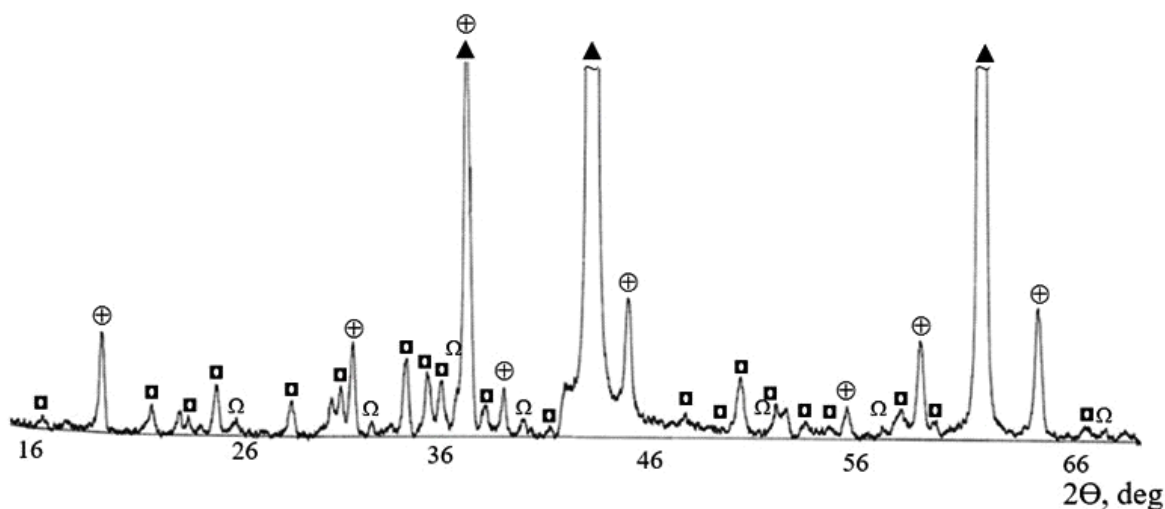
Fig. 2. X-ray diffraction pattern of periclase-spinel samples: ▲ − MgO, ⊕ − $MgFe_{0.2}Al_{1.8}O_4$, ▫ − $CaMgSiO_4$, Ω − $FeTi_2O_5$

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with an indefinite structural type, but with the cubic syngony, which results in a high degree of isotropy of the thermophysical properties and is positively reflected in the thermal stability of the material. Phase decomposition is caused by rapid supersaturation of the divalent cationic sublattice of the mixed type solid solution, which leads to an increase in structural distortions due to the larger radius of the trivalent cations. However, the phase decomposition of solid solutions also favorably affects the thermal stability of the material, since a significant amount of nanodispersed neoformations arise and their interfacial boundaries are able to effectively dissipate the energy of thermal cracks. Cationic vacancies, generated during iso- and heterovalent isomorphism occupying 2, 3, and 4 valence cationic sublattices of solid solutions, are also of great importance; they ensure additional degrees of freedom to the elements of the crystal lattice, in fact, damping thermomechanical stresses during thermal shocks. The mechanism of generation of cation vacancies can be illustrated by a simple example:

$$3Mg^{2+} \rightarrow 2Al^{3+} + Va.$$

Undoubtedly, the noted effects of structural-phase adaptation of periclase-spinel refractory to high-gradient thermal loads are provided by other new principles for organizing a fragmented, micro-cracked structure of a material due to the conjugation of solid-phase exchange reactions with the establishment of a mobile equilibrium when the temperatures of a stationary state are reached. The possibility of phase inversion of spinel solid solutions up to a change in the type of spinel structure is also important; in particular, of quandilite:

$$2MgO \cdot TiO_2 (type «2-4») \leftrightarrow MgO \cdot Ti_2O_3 (type «2-3»),$$
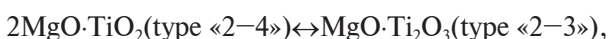
where the type of spinel structure reflects the oxidation state of Mg and Ti.

The formation of specific nanosized porosity (diffusion pores due to the Frenkel effect) is also important, which alternates with diffusion creep of grain boundaries (due to the Kirkendal effect) under sign-variable temperature conditions of production and thermal cycling due to differences in the sizes of diffusing cations, which causes thermoplasticity of the modified matrix phase.

Electron microscopic analysis confirmed the feasibility of the noted principles for achieving the structural-phase adaptability of a material to thermal shocks. Fig. 3 identifies graphic structures in the form of alternating oriented strips of nanodispersed particles with different phase compositions, which is typical for the isolation of neoplasms during the spinodal mechanism of phase decomposition of solid solutions.
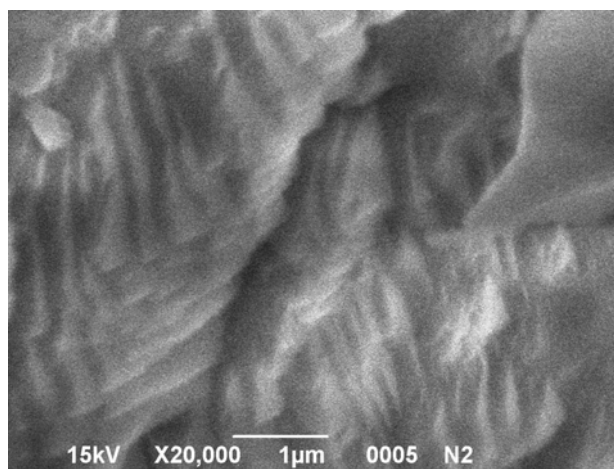

Fig. 3. Microphotograph of a polished section of a refractory sample

Fig. 4 shows microphotographs characterizing the features of the contacts of the particles of the dispersed part of the refractory. It can be seen from Fig. 4a that particles with transverse dimensions of up to 20 μm do not have structural concentrators of thermomechanical stresses in the form of straight edges, sharp corners, microcracks, and chips. The particle in the center of Fig. 4a is not completely insulated and has at least two contacts that provide integrity and strength to the microstructure at normal temperature.

On the left side of Fig. 4b, the contact bridge consists of an accumulation of nanodispersed light particles, which are more fusible and provide plastic-sliding mobility. On the right side of Fig. 4b, a visible structure element is observed in the form of a horseshoe or a compressed tube. Through this element, the particle under consideration contacts with two other particles, and the upper one is sintered with the tubular element, and the lower one forms a kind of hinge (the protrusion of the tubular element enters the cavity of the particle, forming a gap with a maximum opening 2 μm). Obviously, at high temperatures, the elasticity of the tubular element will decrease and the viscoelastic properties will increase; this reaction will ensure the redistribution and compensation of thermal stresses due to the shear and rotation of the corresponding particles.

It should be also noted that the degrees of freedom of the particle under consideration are not limited to the particle located to the left of it and above in Fig. 4a, b. This conclusion is confirmed by
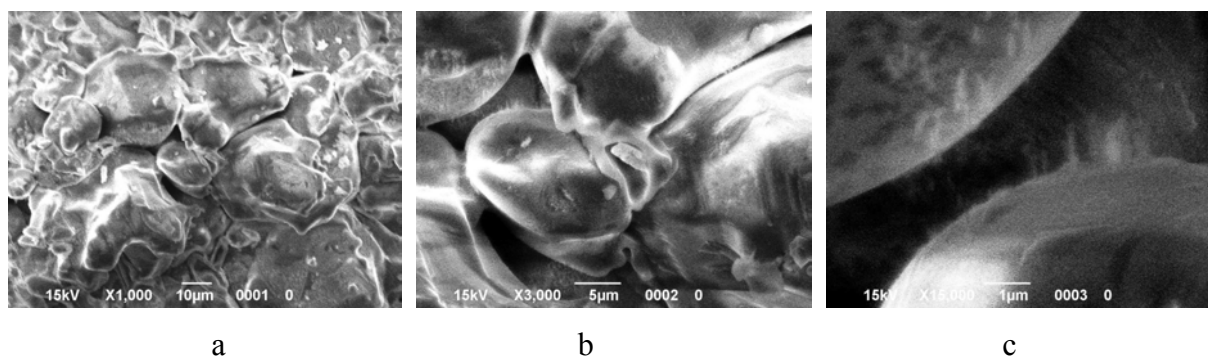
a   b   c

Fig. 4. Typical features of the microstructure of the matrix phase of the refractory

the almost ideally smooth, hemispherical rounding of both particles and the presence of a gap of up to 2 μm at normal temperature (Fig. 4c). These results confirm the ability of the material to effectively counteract sign-variable high-gradient heat waves due to the multiplicative, complex mechanism of structural-phase adaptation to thermal deformations.

Conclusions

Theoretical studies of the subsolidus structure of the $MgO-FeO-Al_2O_3-TiO_2$ system allowed establishing patterns of changes in the thermodynamic stability of phase combinations during melting/crystallization processes. On this basis, the features of solid-phase exchange reactions were predicted, taking into account the information about the existence of a system of solid solutions with different types of crystal structure in certain areas, which made it possible to implement new principles for ensuring thermal stability in the developed refractories. Physical and chemical research methods have confirmed the increased ability of the material to flexibly adapt the phase composition and microstructure to thermal stresses.

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ПРИНЦИПИ ЗАБЕЗПЕЧЕННЯ ТЕРМОСТІЙКОСТІ В ІННОВАЦІЙНІЙ ТЕХНОЛОГІЇ ПЕРИКЛАЗОШПІНЕЛЬНИХ ВОГНЕТРИВІВ

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У даній статті наведені результати дослідження структурно-фазових закономірностей та особливостей поведінки периклазошпінельних вогнетривів в умовах високоградієнтних температурних навантажень. Результати аналізу структурно-фазової мінливості досліджених зразків вогнетривів використані для досягнення заздалегідь заданої термостійкості. На основі дослідження субсолідусної будови системи MgO−FeO−Al₂O₃−TiO₂ зроблено прогноз стосовно особливостей протікання твердофазних реакцій обміну з урахуванням відомостей про існування в окремих ділянках системи твердих розчинів з різним типом кристалічної структури. Це дозволило реалізувати в розроблених периклазошпінельних вогнетривах нові принципи забезпечення термостійкості, а саме організацію фрагментарної, мікротріщинуватої структури матеріалу через поєднання твердофазних реакцій обміну з встановленням рухомої рівноваги при досягненні температур стаціонарного стану. Додаткове значення має можливість фазової інвертованості твердих шпінельних розчинів аж до зміни типу шпінельної структури, зокрема кваділіту. Фізико-хімічними методами досліджень підтверджено підвищену здатність матеріалу гнучко адаптувати фазовий склад та мікроструктуру до термічних навантажень. Електронно-мікроскопічним методом аналізу підтверджено реалізованість зазначених принципів досягнення структурно-фазової адаптованості матеріалу до термоударів.

Ключові слова: периклазошпінельні вогнетриви, термостійкість, герциніт, ульвошпінель, кванділіт, термічна стабільність.

PRINCIPLES OF ENSURING THERMAL STABILITY IN INNOVATIVE TECHNOLOGY OF PERICLASE-SPINEL REFRACTORIES

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This article presents the results of research on the structural-phase regularities and behavior of periclase-spinel refractories under high-gradient thermal loads. The findings from the analysis of structural-phase variability in the refractory samples are used to achieve the desired thermal resistance. Based on the investigation of the subsolidus structure of the MgO−FeO−Al₂O₃−TiO₂ system, predictions were made regarding the characteristics of solid-phase exchange reactions, considering the existence of solid solutions with various types of crystal structures in specific areas of the system. This enabled the application of new principles for ensuring thermal stability in the developed periclase-spinel refractories, specifically through organizing a fragmented, micro-cracked structure by combining solid-phase exchange reactions with the establishment of mobile equilibrium upon reaching stationary-state temperatures. An additional feature is the possibility of phase invertibility of solid spinel solutions, including changes in the type of spinel structure, in particular quandilite. Physicochemical research methods confirmed the enhanced ability of the material to flexibly adapt its phase composition and microstructure to thermal loads. The feasibility of these principles for achieving the structural-phase adaptability of the material to thermal shocks was validated by electron microscopy analysis.

Keywords: periclase-spinel refractories; herzenite; ulvospinel; quandilite; thermal stability.

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