ANNOTATION

dissertation for the degree of Doctor of Philosophy PhD in the educational program 8D07203 "Metallurgy"

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Research and development of technology for obtaining refractory lining with high operational properties for metallurgical units

The relevance of the work

The relevance of the work is determined by the objective need to involve carbon fluorinated waste generated in the production of primary aluminum in metallurgical and energy production as low-cost energy resources and reducing agents.

For example, Kazakhstan Aluminium Smelter JSC (Pavlodar) annually removes up to 1,500 tons of waste from carbon refractory lining of electrolyzers and up to 25,000 tons of burnt anodes with a carbon content of at least 85% by weight, impregnated with components of the cryolite–alumina melts. The content of significant amounts of alkaline cations (Na^+, K^+) in waste, as well as extremely harmful F^- and S^{2-}, does not allow them to be simply stored in sludge storage areas and requires constant expenditures for special storage conditions. A simple and efficient method for recycling such waste is proposed, involving its use in the metallurgical industry as a multifunctional charge component: simultaneously serving as a fuel substitute for expensive and scarce coke, and as a metallurgical slag fluxing agent, whereby alkaline and fluoride salts replace fluorite-based slag modifiers.

The recycling of alkaline- and fluoride-containing carbonaceous waste in the metallurgical and energy industries, instead of its costly storage, will contribute to enhancing the competitiveness of the products and enterprises of the Republic of Kazakhstan, its regions, and individual joint-stock companies. The primary obstacle to such recycling is the reduction in the resistance of the lining of thermal units caused by exposure to alkaline- and fluoride-containing agents released from such waste during processing.

In order to develop refractory materials and products with enhanced resistance to alkaline- and fluoride-containing melts and gases, capable of ensuring optimal resistance of thermal units in the metallurgical and energy sectors during the processing of the above-mentioned waste, it is necessary to investigate the mechanisms of destruction of aluminosilicate refractories by alkaline- and fluoride-containing agents.

Although aluminosilicate refractories with enhanced resistance to alkaline- and fluorinated corrodients had neither been produced nor developed until recently, the theoretical and practical studies conducted have made it possible to approach the solution of this problem from new perspectives.

The subject of the research is aluminosilicate refractories used for lining thermal units and resistant to the effects of fluorinated slags and gaseous phases.

The object of the research is the technology for producing highly dense, chemically resistant aluminosilicate refractories intended for lining thermal units exposed to fluorinated corrodients.

The aim of the work is to analyze the mechanisms of destruction of aluminosilicate refractories by fluorinated reagents (slags and gases) and to develop the composition and production technology of aluminosilicate refractories resistant to fluorinated reagents.

To achieve the set goal, the following tasks were planned:

1. To conduct comprehensive researches of the mechanisms and kinetics of the destruction of aluminosilicate refractories by fluorinated corrodients in metallurgical production.
2. To investigate the physicochemical and technological properties of aluminosilicate refractory raw materials of the Republic of Kazakhstan.
3. To develop the composition and production technology of high-density aluminosilicate refractories based on mineral raw materials of the Republic of Kazakhstan for thermal units processing fluorinated carbonaceous materials.
4. To manufacture and test a pilot-industrial batch of aluminosilicate refractories resistant to fluorinated corrosive agents.

Scientific novelty. For the first time, the study has:

– determined the dependence of the physicochemical processes (mullite synthesis and quartz inversion) occurring under the influence of fluorinated agents within the temperature range of 450–1350 °C on the mineral composition of aluminosilicate raw materials.

– it was experimentally established that the effect of fluorine content on the durability of aluminosilicate refractories is determined by its concentration: small additions act as a mineralizing agent, whereas higher amounts function as a flux through their influence on the rheological and reactive properties of the silicate melt.

– a new technology has been developed for the production of ultra-dense aluminosilicate refractories with enhanced chemical resistance;

– established that the increased chemical resistance of ultra-dense aluminosilicate refractories against fluoride- and alkali-containing reagents (melts and gaseous phases) is due both to the reduction of the interaction surface between the reagent and the refractory and to the processes of secondary mullite formation at the contact boundary.

Practical significance of the work. The possibility of the integrated use of raw materials from the Republic of Kazakhstan for the production of ultra-dense aluminosilicate refractories with enhanced chemical and thermal resistance to fluoride- and alkali-containing reagents of thermal processes has been established.

Compositions and production technology for ultra-dense aluminosilicate refractory products with increased resistance to fluorinated corrodients have been

developed for application in metallurgical and power-generating thermal units using fluorinated waste from aluminum production as fuel. The results of the work have been implemented at «Maker» LLP.

The aluminosilicate refractory products obtained on the basis of the conducted scientific and technological studies may be manufactured at «Kazogneupor» LLP or at any other enterprise producing aluminosilicate refractory products, and may be used at domestic metallurgical enterprises and thermal power stations utilizing fluorinated carbonaceous waste from aluminum production as fuel and reducing agents.

Research methods. The following methods were employed in the dissertation research: X-ray fluorescence chemical analysis, X-ray phase analysis, differential thermal analysis with mass spectroscopic analysis of evolved gases, refractoriness determination, determination of the initial deformation temperature under load, optical and electron microscopy, methods for determining ceramic and mechanical properties (water absorption, open porosity, apparent density, true density, compressive strength), determination of residual dimensional changes upon heating, determination of sinterability, determination of clay plasticity, laser sedimentation analysis of particle size distribution, determination of the binding capacity of clays and kaolins, determination of clay drying sensitivity, and determination of slag resistance.

Provisions submitted for defense:

– the mechanism of destruction of aluminosilicate refractories under the action of fluoride- and alkali-containing corrodients in metallurgical production;

– the charge composition and production technology of ultra-dense aluminosilicate refractories based on raw materials from the Republic of Kazakhstan;

– the results of investigations into the processes and kinetics of interaction between the developed refractories and fluorinated slags.

Research venue. The research work was carried out at the Department of Metallurgy and New Materials of Abylkas Saginov Karaganda Technical University and in the laboratory of the Department of Chemical Technology of Ceramics and Refractories of the Institute of New Materials and Technologies at Ural Federal University named after the first President of Russia B.N.Yeltsin.

Personal contribution of the doctoral candidate to the dissertation.
The author participated in defining the objective of the work and formulating the research tasks, as well as in preparing scientific articles and conference abstracts. The major part of the scientific and practical results determining both the scientific novelty and the practical significance of the work as a whole was obtained personally by the author. The author independently carried out the entire complex of applied studies concerning the mechanisms of destruction in fluorinated corrodients, the investigation of raw materials, the development of compositions and production technology, and the study of the properties of ultra-dense aluminosilicate refractory products.

Approbation of the work. The principal scientific results of the dissertation are reflected in 10 publications:

– 1 article published in a journal indexed in the Scopus database: «CIS Iron and Steel Review» (Russia) — percentile 62;

– 3 articles published in journals indexed in the Scopus database: «Refractories and Industrial Ceramics» (Russia) — percentile 19;

– 3 articles published in journals recommended by the Science and Higher Education Quality Assurance Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan: ("Proceedings of the University, No. 3(88) (Karaganda, Kazakhstan), «KIMS», № 325 (2), № 335 (4) (Almaty, Kazakhstan);

The main results were presented at three international conferences:

– 1 conference abstract at the young scientists' conference «Technogen 2021» entitled «Fundamental research and applied developing of recycling and utilization processes of technogenic formations», (Yekaterinburg, Russia);

– 1 conference abstract at the scientific conference «Actual Challenges of Modern Science» (Pereiaslav);

– 1 conference abstract at the International Conference of Refractories and Metallurgists held in Moscow, Russia.

Based on the results of industrial trials, the following reports were obtained:

– a report on pilot-industrial testing of ultra-dense chamotte refractory products manufactured by «Kazogneupor» LLP in the cupola melting furnace of PZGO LLC;

– a report on industrial trials based on comprehensive investigations of the mechanisms and kinetics of destruction of aluminosilicate refractories by fluoride-containing corrosive agents in metallurgical production under the conditions of «Maker» LLP.

Structure and scope of the dissertation.

The dissertation consists of an introduction, a main body comprising five chapters, a conclusion, and appendices. The dissertation contains 126 pages of text, including 56 figures, 36 tables, and a bibliography comprising 83 references.