Nanomodification of Refractories with Finely-Dispersed Additives with the Use of a Vortex Electromagnetic Homogenizer

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Abstract. The article presents the laboratory and industrial research and the analysis of the impact of modification of refractory concretes and products with finely-dispersed nanomaterials. The dependence of the structural and physical-mechanical characteristics of mullite-corundum refractories of different types (for ladle furnace lances and for supporting blocks of rolling mill carriages) on nanomodification by electromagnetic homogenization is shown. The possibility of using a vortex electromagnetic homogenizer to significantly improve the performance of refractories is shown. In addition, the efficiency of using nanodispersed silicon dioxide is established and its optimal concentration is determined.

1. Introduction

Searching for the possibilities to reduce material costs is one of the key focus areas for steelmaking companies. In particular, improving performance of refractories is an important task both from the perspective of practical application and of metal science. Solving this task will make it possible not only to increase the quality of manufactured products, but also to improve such significant parameters as productivity and profitability. In order to solve the problem, energy-efficient modification of the available refractory materials with the use of various finely-dispersed modifying additives may be applied. At present, such approach is used in many industries. The main remaining problems are selection of the type of a modifying additive and its quantity, and achievement of a high degree of binding material homogeneity.

It is known that small additions (below 1 weight percent) of nanoparticles allow achieving a significant improvement of performance characteristics of products due to their influence on the structure formation processes. It should be noted that the existing methods of modifying high-alumina binding materials, such as mixed grinding in ball mills and nanoparticles injection with the use of suspensions do not give the desired outcome for various reasons: long processing time, particle-particle aggregation, segmentation and subsequent lamination, which is proved by a number of recent works in
this area all over the world. In the recent researches not only alumina and silica nanoparticles, but also such complex compounds as zirconium silicate ZrSiO$_4$ [1–5] have been used. With this in mind, a method of vortex electromagnetic homogenization of the ground stock with the use of a finely-dispersed silicon dioxide additive is applied in this work.

Samples obtained during the work were examined with the use of up-to-date techniques, including: measurement of specific surface area by low-temperature nitrogen adsorption, nondestructive and destructive testing methods to measure ultimate compression strength, density determination and thermocycling.

All investigations were carried out with the use of the vortex electromagnetic homogenizer developed and manufactured by the Research and Production Enterprise Intor (OOO NPP Intor) in collaboration with the department of functional nanosystems and high-temperature materials of the National University of Science and Technology MISIS. This paper presents calculations of operational parameters for VEH-80 (Vortex Electromagnetic Homogenizer-80). Optimal process parameters for operation of the electromagnetic homogenizer, particularly quantity and maximum permissible weight of ferromagnetic rods, the loading density in the active area of the homogenizer, were determined. Optimal processing conditions and their influence on the structure of ceramic samples were established.

2. Input materials

High-alumina calcium aluminate-based binder is used as an input material. This binder is used for manufacture of refractories with addition of other components. The test sample of high-alumina cement is composed of aluminium oxide (69.5 %), calcium monoaluminate (23.5 %) and powder mullite (7.0 %). Particle-size distribution is shown in Figure 1.

![Figure 1. Particle-size distribution of the binder test sample (AIM grade cement).](image)

Average size of the binder particles is within the range from 5 to 10 micrometers. The binder composition based on the results of the X-ray phase analysis is given in Table 1. The content of components may vary within 3-4 weight percent depending on the batch.

Commercially available hydrophilic AEROSIL® 300 with an average particle size of 10 nm is used as nano-sized SiO$_2$ in this research. This material is industrially produced by hydrolysis of a volatile silicon compound in oxy-hydrogen flame. Fine-grain structure of SiO$_2$ is formed during this process. Particles of AEROSIL® 300 may vary from 7 to 40 nm.
Table 1. Chemical composition of the binder.

| Main components | Content, weight fraction, % |
|-----------------|-----------------------------|
| Al₂O₃            | 37.5 – 41                   |
| CaO             | 35.5 – 39                   |
| SiO₂            | 3.5 – 5.5                   |
| Fe₂O₃           | 13.0 – 17.5                 |
| MgO             | Below 1.5                   |
| TiO₂            | Below 4                     |

Special chemical properties of this material are due to the presence of siloxane and silanol groups on the surface of particles. Siloxane groups predominate, which determines inertness of synthetic silicic acid, while silanol groups give the material hydrophilic properties.

Examination of this material with the use of a scanning electron microscope showed that it was composed of aggregates of different sizes ranging from 0.5 to 40 µm. Silicon dioxide structure is shown in Figure 2.

![AEROSIL® 300 micrograph.](image)

The aggregates shown in the micrographs are, in their turn, composed of individual particles from 7 to 40 µm in size, which is proved by transmission electron microscopy. The specific surface area of this material was measured by the low-temperature nitrogen adsorption method. The measured value was 258 m²/g.

3. Nanomodification device

The vortex electromagnetic homogenizer (VEH) is designed to make homogeneous mixtures of ceramic and other nonmagnetic materials with the use of magnetic agitators and rotating electromagnetic field.

The homogenizer VEH ensures high-performance mixing and mechanical activation of ceramic materials due to fast rotation in the running magnetic field of ferromagnetic rods, which ensure mixing in fluidized bed.

Figure 3 shows pictures of the homogenizers VEH (VEH-160 – semi-industrial unit, VEH-80 – laboratory unit)
To process the binder with the use of a finely-dispersed modifying additive, conditions that had been previously determined as optimal and allowing achievement of the most homogeneous particle-size distribution in the volume of material were selected.

A laboratory set of samples with varying content of Aerosil® was produced with the use of this method. Based on the obtained results, a commercial batch of refractory concrete was produced.

The content of the nano-sized modifying additive varied within the range from 0.4 to 1.2 weight percent of the binder weight.

4. Results and discussion

Based on the results of the research, optimal parameters of the modification of refractories for different applications were determined in terms of their influence on physical and chemical properties of refractories. Table 2 shows results of examination of physical and mechanical properties of refractory concretes depending on the nanomodifier amount.

Table 2. Apparent density and tensile strength of samples of concrete for supporting blocks of the rolling mill carriages.

| Sample   | Apparent density after drying, g/cm³ | Apparent density after burning, g/cm³ | Tensile strength after drying, MPa | Tensile strength after burning, MPa |
|----------|--------------------------------------|---------------------------------------|-----------------------------------|-------------------------------------|
| AIM      | 2.65                                 | 2.59                                  | 96.9                              | 138.5                               |
| AIM VEG  | 2.57                                 | 2.50                                  | 82.1                              | 86.9                                |
| 0.4% SiO₂| 2.63                                 | 2.59                                  | 92.1                              | 107.8                               |
| 0.5% SiO₂| 2.66                                 | 2.59                                  | 99.5                              | 147.6                               |
| 0.6% SiO₂| 2.63                                 | 2.60                                  | 95.9                              | 122.7                               |
| 0.7% SiO₂| 2.66                                 | 2.61                                  | 88.3                              | 106.4                               |
| **0.8% SiO₂**| **2.65**                         | **2.62**                             | **115.7**                         | **171.4**                           |
| 0.9% SiO₂| 2.68                                 | 2.64                                  | 100.9                             | 173.9                               |
| 1% SiO₂  | 2.63                                 | 2.60                                  | 118.5                             | 162.1                               |

Optimal concentration of SiO₂ nanoparticles in the samples of concrete amounted to 0.8 weight percent with reference to the weight of binding material (0.04 weight percent of the weight of concrete). A proved increase of the true pycnometric specific gravity of the laboratory samples of 11 and 20 percent
for concretes for blocks and lances respectively was achieved. Strength of laboratory samples after burning increased by 23.8% (for concrete for blocks) and 32.1% (for concrete for lances). Based on the obtained data, optimal process conditions of modification with the use of the vortex electromagnetic homogenizer were proposed for manufacture of trial batches of concretes for supporting blocks of the continuous reheating furnace carriages at the Plate Mill (Rolling Mill-3) (North Cast ABL 70.022) and for manufacture of unshaped concretes for lances for top argon blowing of metal in the ladle of the ladle-furnace North Cast BL 80.023/01. Manufacture of the trial batch and analysis of the results were part of the research conducted in collaboration with PAO Severstal.

The results of the performance tests of the supporting blocks for carriages are given in Table 3.

| Type of supporting block | Average time in operation of supporting blocks, days | Average time in operation of reference blocks for comparison, days |
|-------------------------|-----------------------------------------------|-----------------------------------------------|
| 412                     | 106                                            | 64                                            |
| 414                     | 83                                             | 63                                            |
| 415                     | 136                                            | 72                                            |
| 416                     | 86                                             | 78                                            |

The average life calculated by averaging the values of all 12 nanomodified blocks amounted to 102 days (a 41 % increase).

The results of the performance tests of the ladle-furnace lances are given in Table 4.

| Number of test lance | Life, minutes |
|----------------------|---------------|
| 1                    | 207           |
| 2                    | 183           |
| 3                    | 117           |
| Average value        | 169           |

The average life of the lances amounted to 133 minutes, which means a 27 % increase compared to the average value.

5. Conclusions
Optimal parameters of the modification of refractories for different applications were determined in terms of their influence on physical and chemical properties of refractories. Optimal concentration of $\text{SiO}_2$ nanoparticles in the samples of concrete amounted to 0.8 weight percent with reference to the weight of binding material both for concrete for lances and concrete for carriage blocks.

An increase of the true pycnometric specific gravity of 11 and 20 percent for concretes for blocks and lances respectively was achieved. Strength of final products after burning increased by 23.8 % (for concrete for blocks) and 32.1% (for concrete for lances).

The results of the conducted research and tests suggest that it is possible to improve the performance parameters of refractory products made of unshaped mullite-corundum mixtures by at least 20% due to nanomodification. Industrial application of this technology will ensure a significant economic benefit due to reduction of costs related to purchasing refractory materials and increase of interrepair cycles.
References

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