INTERACTION BETWEEN FIRE-RESISTANT MAGNESIA-DOLOMITIC RAMMING MIXTURE AND OPEN-HEARTH PROCESS MELTS FROM POSITIONS OF DIFFUSION ZONING THEORY

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The purpose of the work is comparative studying of the mechanism of martin furnaces hearth deterioration in use for stuffing the magnesia-dolomitic ramming mixture of Ankerharth and Jehearth marks, received on the foreign enterprises, and magnesia powders of PPM 85 mark of domestic productions. The main problems of researches: studying of diffusive zoning in magnesia-dolomitic materials due to the interaction between materials and metal and slag melts (with application of the theory of reactionary developed by petrologists [1]); revealing of the factors affecting on stability refractory materials during their service. Chemical corrosion during the service is a principal reason of lowering fire-resistant materials stability. We study chemical, phase composition and the structure of samples from various hearth sites of martin furnaces pre- and after service in zones arising at interaction of fire-resistant materials with metallurgical melts. The comparative analysis of these changes and parameters depending on mark of refractory materials was carried out. Hearth samples of martin furnaces were obtained from three metallurgical plants. Fire-resistant mixture of Ankerharth mark (manufacture RHI AG) and of Jehearth mark (manufacture OAO «Slovak magnesia plants») were initial material on OAO «Omutninskiy" and OAO «Vykcunskiy» metallurgical plants. Powders of mark PPM 85 GOST 24862-81 (manufacture of OAO «Combine «Magnesite») was initial on «Chusovskoi metallurgical plant». Methods of optical and electronic microscopy and microprobe analysis, chemical and X-ray phase analysis were used for research.

The chemical and mineral composition of all fire-resistant materials used in martin manufacture bear similarities: they consist of periclase MgO (80-90 %), lime CaO (8-20 %) and impurities of the phases (3-5 %) containing SiO_2, Fe_2O_3, Al_2O_3. Differences between materials compositions lie in its ratio components: in Ankerharth mark mixture it is more MgO and less CaO and, hence, ratio CaO/SiO2 is far above, than in mixture of Jehearth mark. Domestic materials contain approximately as much periclase as foreign ones, but they differ from its by the larger amounts of SiO_2, Al_2O_3 and TiO_2 containing phases. According to our data the most part of iron is represented by Fe_2O_3 (1,8-2,1 %). FeO content is in the range of 0,2-0,4 % in all materials.

In the reactionary zoning columns arising at interaction of fire-resistant materials with metallurgical melts, about 5 zones are allocated. Moderately changed zone 1 is closed to initial refractory material on phase composition. Most cardinal changed zone 5 is almost completely combined by new-formed phases. General thickness of reactionary columns reaches tens centimeters, thickness of its most changed parts - 5-7 mm.

The main feature of changes chemism of refractory material reduces to carrying out from it magnesium and the introduction of iron and silicon, to increase of a role of trivalent iron in relation to bivalent as approaching the contact of the refractory - the melt. Change of mineral composition of a column zones is characterized by increase of ferruginosity of periclase up to 30 % down to its full replacement by magnesioferrite, magnetite and wustite. The aluminates formed in moderately changed zones, silicates of calcium, merwinite and ferrite of calcium – in more changed zones. Boundaries of formed zones are sharp, caused by occurrence or disappearance of any phase. There is a reduction of number of formed phases in the intensity of process direction along zoning.

The phase composition becomes similar for all refractory material in the closest zone to the contact with metallurgical melts. Periclase remains only as relict grains with high ferruginosity up to 30 %, and magnesioferrite, forming large crystals, becomes the main mineral. Magnetite, ferrites of calcium and dicalcium silicate filling intervals between high ferrous phases are presented at smaller amounts. The important feature of structure of 5-th zone on Jehearth material is occurrence of becomes melt ferrous oxide.

Results of the chemical analysis of bi- and trivalence iron in poorly changed zones of a column have shown, that iron is present mainly at a bivalence state. In the least changed (1-3) zones contents of FeO is increased up to 9-10 %, and Fe_2O_3 - decreases up to 0,5 % in comparison with initial mixture. In most intensively changed zones of a column (4-5) contents of FeO is increased up to ~ 24 %, and Fe_2O_3 - up to 42 %, i.e. the trivalence form almost in 2 times prevails above bivalence. Trivalence iron is fixed, mainly, in magnesioferrite, magnetite and ferrite of calcium. Special feature of the reactionary column composition on material PPM 85 is conservation of periclase, merwinite and occurrence of high a titanous phase in intergrowth with dicalcium silicate. Probably, in service conditions it was low temperature melt which presence at a reactionary zone promoted decrease of the refractory stability.

Chemical corrosion of initial fire-resistant mixtures leaded to of numerous fine pores owing to change phase composition and density of a material within each zone. The formation of large and lengthy pores along the boundaries of column zones is the cause of scaling cracks generation, as consequence, breaking of fire-resistant mixtures. The marked regularities are typical for any reaction zoning arising as in technological [2], and natural processes of interaction of two contrast mediums (rock - melt) [3]. They show, that formation of all zones occurs simultaneously and is consequence of one process of diffusion interaction between the metal and slag melts and refractory materials. Sharpness of replacement fronts revealed that the local equilibrium is achieved in each point of the column. Origin of all reactionary zones occurs simultaneously right at the beginning of process, and their growth - is proportional as the process developed. The intensive gain of FeO and loss of MgO near to boundaries of two mediums result in occurrence of a liquid – melt of FeO. The melt development instead of solid phases is connected with change of a chemical composition and is essentially distinct from melting. It is suggested that exactly melt formed in border zones of the interaction column instead of capillary impregnation by metallurgical melt, results to «metallization» a superficial layer of hearth. Formation such melt promotes also to a softening of the refractory material surface and its erosion.

Comparison of properties (phase, chemical composition and structure) fire-resistant materials of foreign manufacture (marks of Ankerharth and Jehearth) during service has shown that both they exhibit equally high resistance in the hearth of steel-making furnace, despite of some differences of their initial phase and reactionary zones composition.

Considerably lower stability of refractory material of domestic production is caused by increased contents of SiO_2, Al_2O_3, TiO_2, resulting to formation of low-melting melt in reactionary sites of hearth. The adverse factor is also the nonuniform structure of powders PPM 85 containing as dust and too large fragments of the material, that results in the greater heterogeneity of composition and properties of in reactionary zones.

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