NEW FORMULATIONS OF FUSED PERICLASE-BASED REFRACTORY MATERIALS FOR THE LINING OF STEEL LADLES

L. V. Mironova,¹ Yu. A. Borisova,¹ Yu. N. Kochubeev,¹ and V. N. Kungurtsev¹

Translated from Novye Ogneupory, No. 3, pp. 9-11, March, 2004.

New formulations of fused periclase-based carbon-containing refractory materials for differentiated use in the lining of steel ladles (bottom, slag zone, and walls) are proposed. The use of new refractory materials made it possible to improve the lining durability from 80 to 100 heats.

At the Magnitogorskii Iron-and-Steel Works Joint-Stock Co. (MISW JSC), until August 2002, the materials that served as the lining of steel-teeming ladles installed in an oxygen converter shop (OCS) were periclase-carbon refractories based on sintered periclase powders containing 97% MgO. These refractories, however, have disadvantages such as rather high porosity, low apparent density, and low durability. Their maximum stability (service life) is typically 80 heats, and the average stability — 60 heats. The increase in steel output and the ever-increasing importance of technologies for heat treatment of steel outside the furnace require the use of high-quality and high-refractory materials for the lining of steel ladles.

To solve this problem one will need a basically new type of refractory based on a high-purity fused periclase powder. Refractory components made from such periclase are known for their enhanced durability which in part is due to the low porosity of the grains of fused periclase and their resistance to reducing carbon attack.

In practice, the quality of periclase powders is evaluated in terms of four major parameters: (i) chemical composition, (ii) crystal size, (iii) open porosity, and (iv) apparent grain density. These parameters in fact control the wear resistance of periclase-carbon refractories. The quality of periclase powders improves with increase in MgO concentration, periclase crystal size, and apparent grain density and, correspondingly, with decrease in grain porosity [1].

To assess the fused periclase quality, precursor powder samples available from three manufacturers were examined. The samples drawn differed in grain color and grain composition. During the course of analysis, the grain and chemical compositions, apparent density, and open porosity were determined; the powders were also examined petrographically, with emphasis on the color characteristics of the periclase grains.

Color and visual examination of the three powdered samples allowed the grains to be classified roughly into five varieties: (i) white and colorless, (ii) bright-yellow, (iii) brown, (iv) gray, and (v) black [2]. All five varieties were present in the three samples. In sample 1, predominant were grains of brown and black color; in sample 2 - light-brown and brown grains with multiple gray and black inclusions, and in sample 3 — white and light-brown grains with occasional gray and black inclusions. The grains, while differing in color, were also appreciably different in chemical composition, apparent density, open porosity, and crystal size (Table 1). The grains of white and light-brown color, predominant in sample 3, displayed superior characteristics. Poor characteristics were found in grains of black and gray color - modest MgO content, rather high concentration of CaO prone to hydration in air, fine-crystalline, highly porous structure of MgO grains $(20 - 50 \,\mu\text{m across})$, low apparent porosity (3.23 g/cm^3) , high open porosity (8.7%) — factors adverse to the quality of the end product.

A fraction analysis of the samples shows that the apparent powder density in samples 1 and 2 tended to decrease with decrease in grain size and, correspondingly, with increase in open porosity (Table 2). In sample 3, the periclase powder was of higher quality, judging from its apparent density and open porosity characteristics. Periclase of fraction less than 1 mm shows the least stable physicochemical properties, its grains exhibit a fine-crystalline, highly porous structure with MgO crystals $20 - 40 \mu$ m across, which renders the product less durable under service conditions. The largest amount of fractions with grain size less than 1 mm is found in samples 1 and 2. To minimize the adverse effect as-

¹ Magnitogorskii Iron-and-Steel Works Joint-Stock Co., Magnitogorsk, Russia.

sociated with the small grain size, it was required of the manufacturers to supply periclase powders with the percentage of fractions less that 1 mm within 10 - 20% (formerly 40%); furthermore, the periclase crystal size should not be smaller than 300 μ m across, and the powder supplied should not contain grains of gray and black color, without detriment to standard stability characteristics. At the time, of the three periclase powders available, only sample 3 could meet these requirements.

Prior to the changeover to fused periclase in June – July 2002 and to the placement of more strict requirements on the precursor periclase powders, the service life (stability) of the refractory walls of steel ladles was 80 heats; with the innovations introduced as was indicated above, the service life improved to 100 heats.

The service conditions for refractory materials in various zones of the steel ladle are never alike and, consequently, the wear rate of the lining in its different parts is never the same; therefore a differentiated approach to the use of different refractory materials will make it possible to reach an optimum lining endurance in various ladle zones and thus to minimize the amount of hot repairs. To adopt this strategy, one will need a whole range of readily available refractories with different properties. A way of solving this problem would be the installation and putting in service of the second dosing and mixing line of a twin plant Eirich (Germany) and a Laies-Bucher 2500 press. The problem with the second line is that it is somewhat different from the first line.

The second dosing and mixing line is similar in design but constructionally different in some respect from the first line that has been installed in a magnesia-dolomite refractory shop (MDRS). The second line offers several advantages over the first line: (i) molding mixtures can be prepared in several regimes; (ii) the accuracy of component dosing by a dosing weighing unit is 0.3%; (iii) optional variants for feeding the components and mixing time are available; (iv) ethyleneglycol can be fed separately in two stages: in different mixing steps additional components can be introduced.

Operational cyclogram (checklist) for the mixer was worked out by the trial-and-error method directly on the production equipment. The mixture was tested for homogeneity by comparing three samples drawn from a single batch: grain composition, bulk density, and carbon concentration in the mixture were examined. The following parameters were controlled both for a single batch and for several successive batches: the concentration of each grain fraction should not deviate from its average value by more than 5%; the concentration of carbon should not deviate from its average value by more than 0.3%; the apparent bulk density should not deviate from its average value by more than 0.04 g/cm³ and should tend to increase with further mixing.

To assess the technological properties of the mixture, the pressed components were visually checked for appearance and tested for apparent density and surface curvature. Based on the inspection and testing results for several regimes of mixture preparation, individual cyclograms on mixture makeup for each type of product were drawn up.

The Laies-Bucher 2500 press is operated manually; all operational parameters are programmed for a specified time interval. During operation, the pressing cycle is effected in a single pressing rate regime. Optionally, nine pressing rates can be selected. The pressing regimes differed in the number of punch back strokes to let the entrapped air out, in pre-pressing regimes, and in the time for holding the green preform under load and after load relief. Optional were also other regime parameters such as the pressing height, mixer speed, entrapped air release, stopping distance of the die, etc.

TABLE 2. Grain Composition and Properties of Fused Periclase

 Powders

Fraction, mm	Grain percentage, %	Apparent density, g/cm ³	Open porosity, %	Periclase crystal size, µm
> 2.5	5.5	3.44	3.1	80 - 1000
2.5 - 1.6	30.5	3.38	3.7	80 - 600
1.6 - 1.0	29.3	3.36	4.5	80 - 600
< 1.0	34.7	_	_	20 - 40
> 2.5	10.3	3.49	2.2	600 - 800
> 2.5 - 1.6	26.0	3.42	3.2	70 - 300
1.6 - 1.0	25.5	3.31	5.6	70 - 300
< 1.0	37.8	_	_	10 - 50
> 2.5	30.0	3.44	2.9	1000 - 1500
2.5 - 1.6	42.6	3.42	3.2	1000 - 1500
1.6 - 1.0	17.8	3.41	3.3	700 - 1000
< 1.0	9.5	_	_	50 - 100

TABLE 1. Characterization of the Grains of Fused Powdered Periclase

New Formulations of Fused Periclase-Bas	ed Refractory Materials

A Grain color d	Apparent	Open poros ity, %	Mass fraction, %					Crystal	
	density, g/cm ³		MgO	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	$\Delta m_{\rm calc}$	size, μm
White	3.47	2.3	97.02	1.68	0.63	0.18	0.49	0.12	1000 - 5000
Light-brown	3.47	2.6	97.10	1.27	0.85	0.21	0.58	0.29	> 500
Brown	3.38	4.9	95.40	1.97	1.45	0.26	0.92	0.25	50 - 1000
Gray	3.35	5.4	94.34	2.62	1.74	0.38	0.93	0.43	> 1000
Black	3.23	8.7	94.53	2.86	1.03	0.40	1.17	0.50	20 - 40

	Proc	Products			
Characteristic	domestic (MDRS)	purchased			
Lining	7				
Durability, number of heats:					
walls (PUPK-S)	104.2	92.5			
slag zone (PUPK-Sh)	46.9	42.9			
bottom (PUPK-D)	47.5	42.5			
Residual thickness, mm:					
walls (PUPK-S)	80 - 100	80			
slag zone (PUPK-Sh)	70	60			
bottom (PUPK-D)	120	90			
Wear rate per heat, mm:					
walls (PUPK-S)	1.0	1.3			
slag zone (PUPK-Sh)	2.8	3.3			
bottom (PUPK-D)	3.8	4.9			
Produc	ets				
Open porosity, %:					
walls	2.5	5.2			
slag zone	2.5	4.8			
bottom	3.1	4.1			
Compressive strength, MPa:					
walls	48.7	32.1			
slag zone	44.9	35.2			
bottom	51.8	39.3			

TABLE 3. Durability of the Lining of OCS Steel Ladlesand Characterization of Periclase-Carbon Products

To assess the product quality, the pressed preforms were examined for uniform density throughout the height; for surface curvature, for the internal structure of the preform, for the absence of pressing cracks. During the course of tests, individual pressing regimes were specified for each type of product.

In each case, the mixtures were analyzed for graphite content. As is known, the increase in carbon improves slag resistance and refractoriness; simultaneously, the mechanical strength and resistance to oxidation undergo degradation [3]. For this reason, the required amount of carbon is determined by specific service conditions. Mixtures for the refractory lining for use in different zones of the steel ladle were formulated. Based on the results of laboratory and industrial tests, the optimum carbon concentrations for the ladle's refractory lining are: bottom, 5 - 7%; slag zone, 10 - 13%; and walls, 8%. Currently, only refractories of domestic production are used for the ladle lining; their characteristics, compared to those of refractories from a foreign manufacturer, are given in Table 3. The production cost for domestic refractories is about 38 roubles/ton steel.

CONCLUSIONS

Based on the results of laboratory and industrial tests, methods of fabrication of the refractory lining for differentiated use in steel ladles (bottom, slag zone, and walls) have been developed and formulations for carbon-containing refractory materials (a total of 11) proposed.

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