Improvement of Methods of Fused Periclase Crystal Size Determination

L. M. Akselrod, I. G. Maryasev, A. A. Platonov, D. R. Melnikova

A novel objective method of digital analysis for microscopic examination of structural elements of fused periclase was developed. Main parameters are presented, which show the difference of the newly suggested method of investigation from the usual linear one, in which the examination is done with the help of chords. For comparison there are given results of measurements (done with the tools of the old and the new method) of fused periclase crystal size, produced by Magnezit Group and by other manufacturers. Testing of fused periclase containing more than 97,5 % MgO and various ratio of CaO/SiO_2 in periclase-carbon refractories has not found influence of this parameter on the strength of refractories in steel-teeming ladles.

1 Introduction

The quality of refractory materials, produced with application of fused and sintered periclase, depends on a number of characteristics of the latter. It was found out that the size of periclase crystals – in addition to its chemical composition, composition of phases, located between crystals, apparent density – plays considerable role. As it was proved in practice, that the size of crystals exerts considerable influence upon wear resistance of bricks, produced with application of periclase, first of all of periclase-carbon refractories, which are widely used in steel production [1, 2, 3].

Maximally exact evaluation of crystals size in quantitative forecast is necessary not only for choosing periclase of this or that quality for the production of refractory materials, but also for the control of technological factors during production of fused periclase.

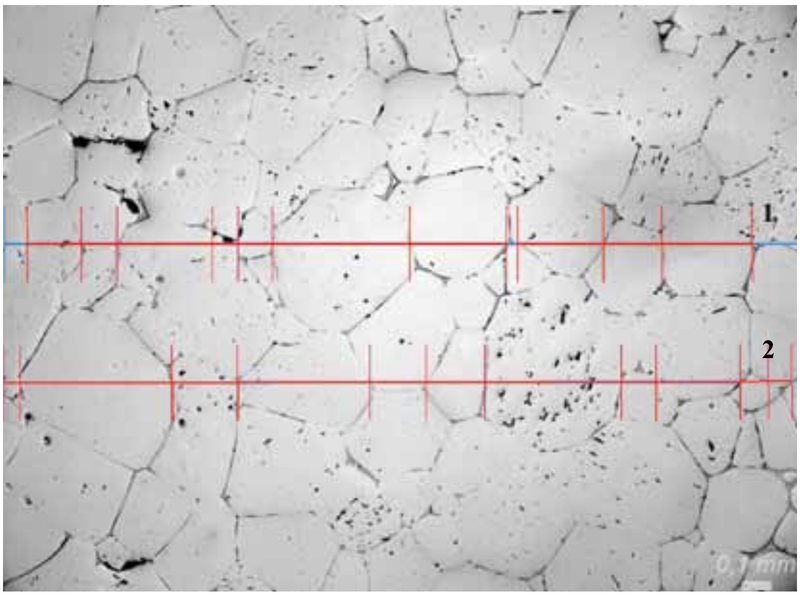

Fig. 1 **A site of fused periclase; size of separate crystals, found out in the microscope eyeglass field, was evaluated by method of intersected lines (chords). Reflected light; magnification: 25×. Section lines were chosen for measuring 1 and 2.**

Determination of chemical composition and apparent density are standardized while determination of crystal size is done with the help of various procedures, that is why precision of results, obtained in different laboratories, is often not the same [1, 2]. It is related both to the difficulty of choosing a representative sample for the investigation and to discrepancies in applied methodologies. It is known, that for melt crystallization products (including periclase) there is a logarithmic normal law of crystal diameters distribution.*

Quantitative evaluation of crystals size distribution is related to obtaining and analysis of considerable statistical material, permitting to establish a distribution law [4].

There are a number of methods for quantitative assessment of crystal size (grains) in metallographic samples on the basis of random sampling. As other quantitative methods they are based on the presentation of a limitlessly large number of intersections of grains with parallel planes or on overlaying onto images of calibrated nets of certain size. Theoretical basics of the methods are given in detail in [5].

*Under the term "periclase crystal diameter" we understand average crystal size, average between the length and the width of a crystal, analogously to the term "periclase crystal size".

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Keywords: periclase, microscopy

But stereometrical methods (developed in the last century) for microscopic analysis of crystals require continuous time for description and are rather labour intensive. Quantitative assessments and calculations of microstructure elements on polished sections or metallographic sections were previously done visually during viewing directly in the microscope eyeglasses.

2 Linear method of assessment

Linear sizes were first measured in divisions of eyeglass scale. Then the obtained results were multiplied for the division value. It was necessary to use during analysis various magnifications from 10× up to 500×, as inadequate magnification in quantitative analysis often brought to erroneous results in assessment of two-dimensional structure parameters as a consequence of detection of new small crystals (grains) under high magnification [4]. Technology of the most widely used "manual" linear methodology of crystal size determination by way of random chords consists in the following:

- Selection and preparation of samples for investigation:
  - Visual evaluation of the total sample and classification of lumpy periclase by colour, structure, texture and crystalline particles size with determination of share of each periclase class.
  - Preparation of samples for investigation. If periclase is in the form of large lumps, it is sawn along the chosen plane, ground and polished. Lumps of periclase less than 10 mm in size are preliminary coated with epoxy resin, then ground and polished.
- Methodology of microscopic investigation:
  - Adjustment of microscope for 100× magnification with the help of eyeglass.
  - Installation of polished sample into holder on microscope table. The first site in the periclase sample is chosen and image is focused.
  - Displacement of the sample to the edge of the line of one crystal from the edge of the net.
  - Determination of crystals size, crossing the line (Fig. 1). If crystals possess isometrically rounded shape, then one of its middle diameter is measured. If the shape of crystals is elongated, then average size is determined: average value between the maximal length and width of the grain.
  - After finishing analysis of a certain fragment the microscope table is displaced lower on the line parallel to the previously investigated site in order to measure another part of the sample and to repeat the process up to the end of the sample edge.
  - In order to determine average crystal size it is necessary to assess the size of not less than 250 crystals.
  - For calculation of final average crystal size the following equation is used:

    $S_{cp.} = s/n$, where

    $S_{cp.}$ – average crystal size (µm),

    s – sum of crystals size (µm),

    n – number of examined crystals (pcs).

Methodology of grid application (ASTM Norm E 112-96/2004) and a number of other methods can be considered as more or less perfected variants of linear method.

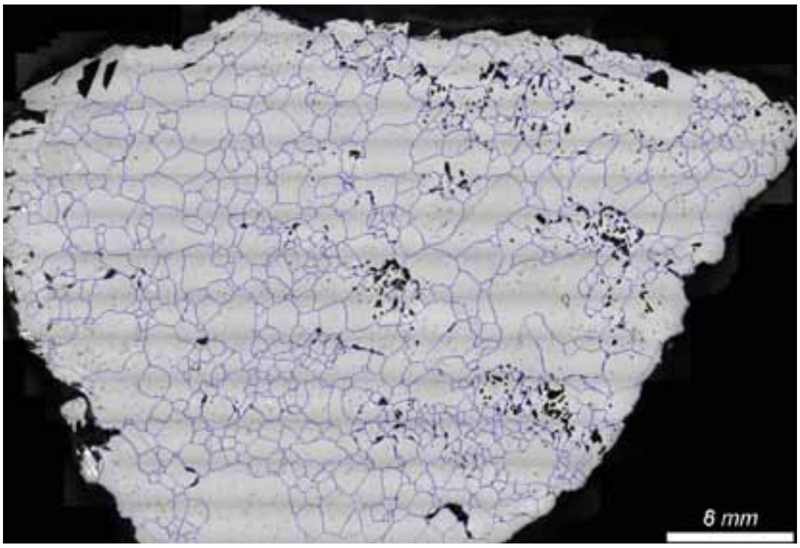


Fig. 2 Example of assessment of the surface of periclase crystals along the whole surface of polished section. Reflected light; magnification: 4×

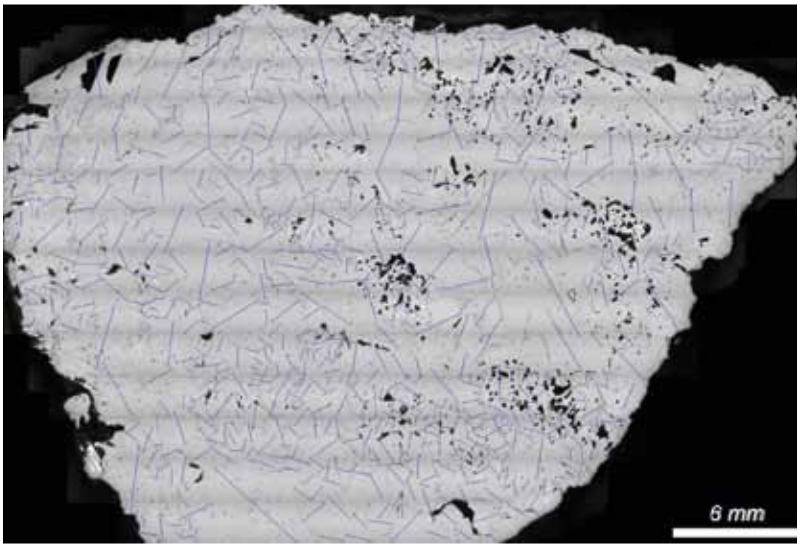


Fig. 3 Example of assessment of the surface of periclase crystals along the whole surface of polished section. Reflected light; magnification: 4×

3 Digital method of crystals assessment

Modern methods of microscopic investigation allow to obtain more reliable and exact results in shorter time. At Magnezit Group Ltd. the equipment of the existing optical microscope Axioplan with a system of digital analysis allowed to modify and to supplement methods of determination of

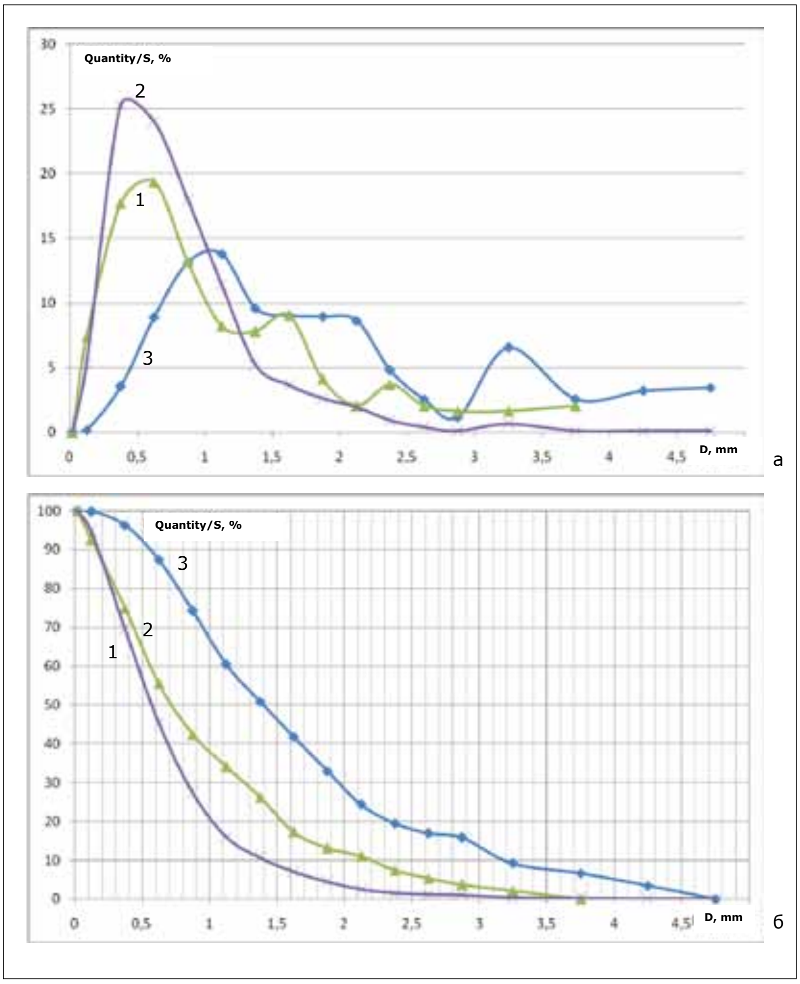


Fig. 4 a–b Curves of distribution of crystal sizes in fused periclase: a – differential curve of distribution of crystal sizes, b – integral curve of distribution of crystal sizes. 1 – old method of chords, 2 – new method of general analysis, distribution by number of crystals, 3 – new method of general analysis, distribution along the surface of crystals

microscopic parameters of refractory materials and raw materials.

The essence of the suggested method consists in modeling of a digital image with large area of polished section 1200–1500 mm^2, under any necessary magnification, embracing its whole plane. After formation of an image is finished, evaluation of geometric parameters of two-dimensional structure is done with the help of special software, in particular of the software Image-Pro Premier by the company Media Cybernetics.

During investigation of fused periclase distinct notion about crystals shape in typical polished sections is obtained and size and surface of all the crystals, which are found in the image (Fig. 2 – 3) are determined. A typical number of measured crystals for fused periclase is from 600 – 1200 depending on crystal size. After measurements are finished, statistical treatment of data takes place and the maximal, minimal and average crystal size are determined, as well as graphs of sizes distribution are drawn with evaluation of parameters D_{10}, D_{50} and D_{90} (where figures mean crystal size corresponding to 10, 50 and 90 % share of crystals, which are less than a certain diameter). For comparison data on character of crystal size distribution in fused periclase, produced by Magnezit Group, are presented. The size was determined by two methods: the "old" one and the "new" one (Fig. 4). By data, given in the Tab. 1 one can see, that method of microscopic analysis with the help of chords (the old method) gives overstated values of crystals size (especially by the item D_{90}), which differ from the real size of all the crystals.

Positive results after introduction of the new method consist in the following:

- Visualization of obtained results.
- Possibility of control and repeated checks.
- Organization of electronic data bases and accumulation of statistics.
- Possibility to do on one and the same image measurements of not only crystals size, but of any basic geometric parameters of plane structure, such as, for example:
  - surface of a separate particle and total surface of contacts,
  - diameter of a spherical particle,
  - dihedral angle between facets,
  - number of microparticles in a unit of volume,
  - number of contacts and other.
- Measurements of crystals size directly on one and the same image allow to obtain precise data on size of very large crystals, which don't fit entirely in the microscope eyeglass field. Previously it was necessary to move the microscope table several times during measurement of such crystals. Now there appeared possibility to obtain precise data on the elements with sharply different linear size, while previously it was necessary in such a case to change microscope magnification during measurements of small crystals.
- When digital methods are used in microstructural analysis, reliability and objectivity of obtained results increase. Good repeatability of data is ensured and influence of human factor decreases. Such results are achieved thanks to increase of amount of data retrieval as well as thanks to retention in real time of all the measurement results. It is possible to assess the obtained result at any moment and if necessary to introduce corrections into determined structure parameters.

All the grades of fused periclase – standard products, manufactured by Magnezit Group – were studied with the help of the new method of crystals size determination. Mineral and chemical compositions were studied as well. Obtained results for some of the grades are presented in Tab. 2.

Techniques were developed, allowing to change fusion mode parameters during production of fused periclase of one and the

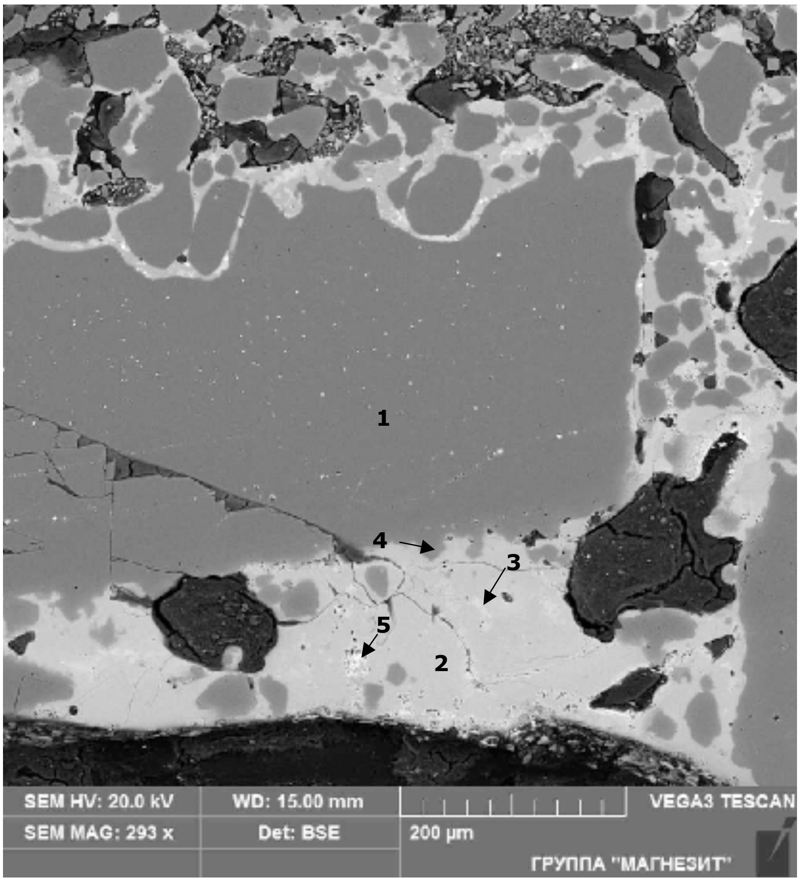
Tab. 1 Example of parameters values characterizing crystals size of fused periclase

Item	Values	
	New Method	Old Method
Surface area of the studied polished section [mm]	651	–
Number of crystals on the surface of polished section [pcs]	767	250
Size of crystals of fused periclase (min-max) [µm]	50–5090	50–3910
Average size of crystals, calculated by the number of crystals[µm]	824	1115
Average size of crystals, calculated by occupied surface [µm][1]	1792	–
Size of crystals D_{10} [µm][2]	180	180
Size of crystals D_{50} [µm]	575	720
Size of crystals D_{90} [µm]	910	2170
Size of crystals DS_{10} [µm][3]	560	–
Size of crystals DS_{50} [µm]	1400	–
Size of crystals DS_{90} [µm]	3270	–

[1] $D_{cp.} = \sum(Si*Di)/\sum Si$, where Si = surface of crystal, Di = average diameter of crystal.
[2] D_{10} = 10 % of crystals are less than a given size; D_{50} = 50 % of crystals of a given size; D_{90} = 90 % of crystals are less than a given size
[3] DS_{10} = 10 % of the surface of the polished section are crystals which are less than a given size; DS_{50} = 50 % of the surface of the polished section are crystals which are in size as the crystals of a given size; DS_{90} = 90 % of the surface of the polished section are crystals which are less than a given size

Tab. 2 Different parameters of various grades of fused periclase, manufactured by Magnezit Group

Name of Item	Grades				
	Imported 98CS	DTMF 97CS	DTMF 98CS	DTMF 98	DTMF 98,5CS
Average size of crystals calculated by the number of crystals [µm]	768	869	1077	901	801
Average size of crystals calculated by occupied surface [µm]	3288	3458	2779	2137	2168
Size of crystals of fused periclase (min-max) [µm]	48–8200	80–10 200	70–7150	110–7360	60–5280
D_{10} [µm]	160	180	200	240	170
D_{50} [µm]	550	560	900	700	550
D_{90} [µm]	1450	1300	1750	1340	1120
DS_{10} [µm]	910	620	900	640	540
DS_{50} [µm]	2340	2650	1910	2240	2520
DS_{90} [µm]	5620	6100	5150	5140	5320
Mineral Composition [vol-%]					
Periclase	97–98	97–98	97–98	97–98	>98
Monticellite	–	–	–	<1	–
Mervenite	–	≤1	<1	1–2	≤1
Belit	2–3	1–2	1–2	–	1–2
Chemical Composition [mass-%]					
MgO	98,26	97,44	98,09	98,17	98,66
Al_2O_3	0,05	0,11	0,17	0,15	0,13
SiO_2	0,42	0,60	0,44	0,54	0,34
CaO	0,89	1,45	1,07	0,89	0,72
Fe_2O_3	0,38	0,41	0,24	0,27	0,12
Σ	100,0	100,0	100,0	100,0	100,0
CaO/SiO_2	2,12	2,60	2,43	1,65	2,12
Bulk specific gravity [g/cm³]	3,52	3,48	3,52	3,51	3,52



1 – periclase		2 – monticellite		3 – mervenite		4 – AMS		5 – spinelid	
oxide	[mass-%]	oxide	[mass-%]	oxide	[mass-%]	oxide	[mass-%]	oxide	[mass-%]
MgO	98,58	MgO	23,98	MgO	13,37	MgO	24,13	MgO	26,16
Al_2O_3	0,46	SiO_2	39,15	SiO_2	39,45	Al_2O_3	68,84	Al_2O_3	13,74
SiO_2	0,07	CaO	32,86	CaO	44,68	SiO_2	0,33	SiO_2	1,71
CaO	0,21	MnO	3,52	MnO	1,37	CaO	0,22	CaO	1,60
MnO	0,51	Fe_2O_3	0,49	Fe_2O_3	1,12	TiO_2	0,73	TiO_2	0,64
Fe_2O_3	0,17	Σ	100,00	Σ	100,00	Cr_2O_3	1,37	MnO	44,12
Σ	100,00					MnO	3,27	Fe_2O_3	12,03
						Fe_2O_3	1,11	Σ	100,00
						Σ	100,00		

Fig. 5 Microstructure of the working zone of a sample of periclase-carbon brick after service. SEM; detector BSE; magnification: 293×
Washing out of grains of fused periclase from the refractory with formation of new phases – silicates, Al-Mg spinel (AMS) and complex spinelids

same composition, to change within certain limits average size of crystals and, accordingly, specific surface of the whole number of crystals.

Proceeding from the fact that corrosion of periclase crystals surface takes place, it is feasible to compare specific surface of the whole number of crystals, but not the average size of crystals.

4 Evaluation of the influence of CaO and SiO_2 ratio

With the aim of evaluation of the influence to the quality of fused periclase with various CaO and SiO_2 ratios fused periclase of the grades DTMF 98 and DTMF 98CS was tested, which are the main components during production of periclase-carbon refractories for slag line lining of 130-tons steel-teeming ladles.

The ladles operate in a workshop with 100 % treatment of metal in ladle-furnace. 60–70 % of the produced metals are treated in VOD vessels. Metal is cast by continuous casting machine. Basicity of the slag in the steel teeming ladle is between $1,8 < (CaO + MgO/SiO_2 + Al_2O_3) > 2,0$.

Material constitution of bricks: basis-fused periclase of fraction 0–6 mm, 8 % graphite, antioxidant metal Al, Carbores P and phenol-formaldehyde binder. Physical and chemical properties of manufactured bricks both after thermal treatment and after coking are identical. Bricks for slag line were tested at one and the same plant with random selection of slag lines alternation in order to avoid influence of technological metallurgical factors.

Coarse grained periclase containing >97,6 % MgO was used. In the capacity of grain boundary phase certain amounts of monticellite (t_{fusion} = 1500 °C) and mervenite (t_{fusion} = 1575 °C) was used for the grade DTMF 98 and mervenite (t_{fusion} = 1575 °C) and belit (t_{fusion} = 2130 °C) for the grade DTMF 98CS (Tab. 2).

The process of periclase-carbon lining wear in metallurgical vessels takes place according to the known scheme:

- Oxidation of carbon component of the refractory with enlargement of pores. Large ramified pores appear. They communicate with each other. Oxidizing and reduction processes taking place inside refractory also add their share as well as processes providing for removal of gaseous products from reaction zone of the refractory (from the pores of the refractory) during out-of-furnace treatment of metal in the ladle;
- Slag goes along formed pores-channels, in which there is no carbon, and comes into contact with periclase grains: both with coarse-grained and fine-grained aggregates;
- Grains of periclase are subjected to corrosion along the surface of contact with formation of secondary silicates, spinelids and others. At the same time washing out of grains from the structure takes place. It is confirmed by presence of periclase grains in the slag contacting the working surface of periclase-carbon refractory (Fig. 5).

One can suppose, that the final stage of refractories wear has mechanical character and the speed of washing out of periclase grains from the oxidized refractory prevails over the process of slag interaction with components in the intercrystalline space. This version has been checked. It is also possible to suppose, that mervinite and monticellite freed during grinding of the periclase of DTMF 98 grade with CaO/SiO_2 ratio <2 (in the fraction 0–1 mm) can additionally prevent oxidizing of carbon together with the ash from graphite, possessing the melting point lower than the temperature of heating of the refractory in the working area, which contacts with liquid metal and slag. They (mervinite and monticellite) are in pores in liquid phase.

Wear resistance of slag lines during application of periclase of grades DTMF-98 and DTMF-98CS turned out to be the same, and the residual thickness of walls was within the limits of 60–80 mm. In case of application of fused periclase with a density close to 3,50 g/cm^3 and a content of low-melt monticellite and mervinite totaling to 2,5 % one has not shown considerable influence of their amount onto the process of interaction of metallurgical slag of basic composition in steel-teeming ladles with periclase-carbon refractories in comparison to the case, when more high-melting belit occurs in intercrystalline space. In the investigated case the difference in the average size of crystals and in specific surface area of all the crystals of fused periclase of the grades DTMF 98 и DTMF 98CS didn't influence wear resistance of refractories. At present periclase-carbon refractories for steel-teeming ladles and electric arc furnaces are manufactured at Kombinat Magnezit (part of Magnezit Group) with application of coarse grained periclase of the own production. CaO/SiO_2 ratio in fused periclase is determined, but has no decisive influence.

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