FORMATION OF A TRIDYMITE STRUCTURE IN DINAS REFRACTORIES FOR COKE OVENS

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Failure of dinas refractories in coke batteries occurs as the result of chemical interaction of the components with molten slags, salts, and gases, the action of high temperature, and thermochemical loads.

With a total coke battery service life of 25 years and more individual elements of them fail more rapidly, requiring premature repairs. These elements include the roof, the hearth, the heads, and the extreme vertical flues of the coking chambers. Early failure of the lining in these elements of the oven is caused by the special service conditions accompanied by cyclic temperature changes and also by the quality and structure of the dinas parts and therefore an increase in their properties is a pressing problem.

The wear of dinas refractories in the partitions of coke batteries depends not only upon their physicoceramic properties but also upon the necessary stable structure formed in all stages of production and especially in firing.

In analyzing means of development of technology for dinas refractories several nonconformances between the parameters and standards of quality of the compounds and the conditions of rapid firing of parts in tunnel kilns may be noted. A consideration in chronological order of the sequence of change in the production parameters and their influence on part quality is of practical interest for selction of promising production and thermal engineering solutions applicable to the conditions of firing of parts in tunnel kilns.

Based on service conditions in the partitions of coke ovens dinas parts must have low additional growth at 1450°C, a small quantity of residual quartz, and high tridymite. In other words, for an increase in the quality of dinas parts with a high degree of degeneration of quartz existing standards for addition of mineralizing additions to them must be reconsidered.

In [1], which is devoted to high-temperature synthesis of tridymite, production methods making it possible to prepare parts with a high degree of degeneration of quartz by addition to their composition of a large quantity of active mineralizing additions and firing at 1550°C are shown. The fundamentals of this method are partially realized in the production of low-looseness high-temperature fired dinas for the high-temperature zones of blast furnace hot-blast stoves, the increased life of which was the basis of wide use in blast furnace hot blast stoves [2].

Dinas parts with a high iron oxide content may not be recommended for service in coke ovens since an increased content of iron oxides may promote reduction of silicon dioxide to its monoxide in the presence of carbon-containing gases. For dinas parts with a high tridymite content and a low share of residual quartz new methods similar to those used as the basis for the production of low-looseness dinas but with the addition to it of active additions eliminating the reduction of silicon dioxide to the monoxide are necessary.

In this article the rules of the physicochemical fundamentals of the technology for high-tridymitized dinas parts for coke ovens and the results of its use in Krasnoarmeisk Dinas Plant are considered.*

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Fig. 1. Character of the structure of tridymite crystals in dinas.

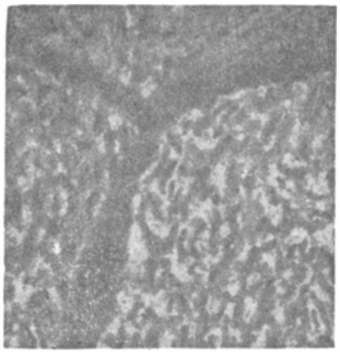

Fig. 2. Microstructure of β-cristobalite.

In tridymite-cristobatility part concretions of trodymite crystals predominate in the fine-grained portion (<1 mm) and cristobality and residual quartz in the grains of former quartzite (>1 mm). Such a heterogeneous structure of the dinas is the result primarily of transformation of quartz in the fine-grained portion under the action of the mineralizing additions and, on the other hand, in the quartzine grains in the absence of them. Each of the crystalline varieties of silicon dioxide determines the properties and behavior of the dinas refractories in service. The most stable form of silicon dioxide in dinas for coke ovens is crystals of tridymite, which broadens the temperature boundaries of its heat resistance from 1470 to 200°C. In the fine-grained portion of dinas tridymite is normally spear-shaped twins forming a concretion (Fig. 1) [3, p. 144].

Under the action of molten silicate tridymite crystals originate in the peripheral shells of the quartzite grains with crystallization in the form of platelets, needles, and prisms. The quantity and form of the tridymite crystals depend upon the original grain composition of the mixture, the composition of the mineralizing additions, and the heat treatment of the parts.

Depending upon the production parameters the ratio of the high-temperature modifications of silicon dioxide in dinas may be different. In production high-temperature fired parts residual quartz normally appears only in the center of coarse grains, transformation of silicon dioxide in which occurred primarily in the absence of the action of molten silicates. In the former quartzite grains the accompanying modifications may be unstable metacristobalite, stable cristobalite, and quartz. In contrast to tridymite a different structure is characteristic of cristobalite crystals (Fig. 2) [3, p. 264].

The advantage of dinas with a tridymite structure includes broadening of the temperature boundaries of its stability as the result of the presence in the structure of concretions of tridymite, which are a unique reinforcing materials. Acceleration of transformation of quartz into dinas and the formation in it of a tridymite structure may be controlled by the temperature of formation of the molten silicates promoting inversion of quartz in its high temperature modification.

The mineralizing additions added to the dinas, calcium and iron oxides, interact in firing with silicon dioxide and form molten silicates. Iron oxides posses different proper-

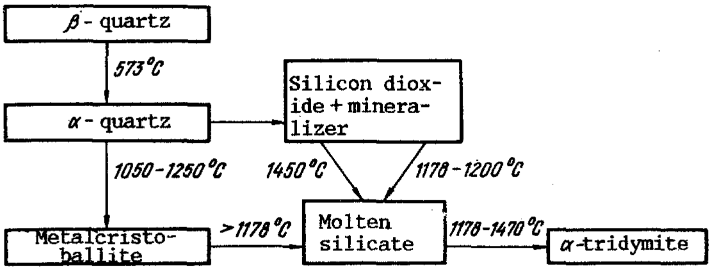

Fig. 3. Plan of the mechanism of transformation of quartz into tridymite.

ties and melting points. For example, FeO is a basic oxide and Fe_2O_3 an amorphous one [4, p. 21]. FeO melts at 1370°C and Fe_2O_3 and magnetite (Fe_3O_4) at 1560 and 1590°C, respectively. The most active form of iron oxides promoting early appearance of molten silicate, is the ferrous form. According to the data of [5, p. 50] in the FeO–SiO_2 system molten material appears at 1178°C and in the Fe_3O_4–SiO_2 system at 1452°C.

The plan of the mechanism of transformation of quartz into its high-temperature modification (tridymite) is shown in Fig. 3 [6]. From the plan it follows that in the absence of interation of molten silicate α-quartz first transformations into metalcristobalite, which then under the action of the molten material recrystallizes into α-tridymite. The composition of the mineralizing additions, the reducing medium, and the temperature of appearance of the molten material have a significant influence on recrystallization. With addition to the dinas of mineralizing additions with a composition of 2-3% CaO+0.6-1% Fe_2O_3 molten silicate appears only at 1452°C while with addition of 2-3% CaO+2% FeO the temperature of appearance of molten silicate drops to 1178-1200°C. From this it follows that with the addition to dinas of Fe (III) the temperature of the appearance of molten silicate is higher than the temperature reached in firing of dinas in 243 m tunnel kilns while, on the other hand, with the addition to dinas of Fe (II) molten silicates are formed in the stages of the end of the heating zone and in the hold, determining the activity of recrystallization of quartz and metacristobalite into α-tridymite.

In the pyrite-roasting residues and converter slags used as the iron mineralizer the iron oxides primarily contain Fe (III) and therefore to improve the physicoceramic and structural properties of dinas for coke ovens it was decided to replace the pyrite-roasting residues and iron scale sludge with material primarily containing Fe (II). Samples of Chelyabinsk Metallrugical Combine converter sludge and Donetsk Metallrugical Plant scale used in laboratory and production investigations contained 77.1% Fe_2O_3 and 8.59% FeO and 32.3% Fe_2O_3 and 56.1% FeO, respectively.

Under laboratory conditions converter sludge was added to Pervouralsk quartzites and scale to Ovruch quartzites. The normal physicoceramic properties of parts specified by Industry Standard 14-41–78 for dinas parts for coke ovens and the structure determined by petrographic investigations of the mineral composition of the dinas were used as the criterion of quality of the dinas parts.

With the use of Pervoural'sk quartzites mixtures with a grain size of not more than 3 and 1 mm were used. A lime-iron addition with a composition of 4% CaO+1% Fe_2O_3 was added to the mixture. With the use of a mixture with a grain size of not more than 1 mm the influence of the added sludge on the mineral composition of the fine grained portion of the dinas in relation to heat treatment conditions was established.

Laboratory specimens were pressed under a pressure of 50 N/mm^2 from mixtures with a moisture content of about 5.5% to an apparent density of 2.20 and 2.10 g/cm^3, respectively, for mixtures with a grain size of ≤ 3 and ≤ 1 mm. After drying the specimens were fired in a batch furnace for a total time of 100 h, including a 28 h hold at 1400 and a 12-h hold at 1450°C.

The physicoceramic properties and mineral composition of the dinas specimens are given in Tables 1 and 2. The properties of the dinas, with the exception of density (charge II, fired at 1400°C), completely satisfy the requirements of Industry Standard 14-41–78 even with the addition of 4% calcium oxide and the temperature of deformation under a load of 0.2 N/mm^2 of the specimens increased to 1660-1670°C.

TABLE 1. Characteristics of the Dinas Specimens from Pervouralsk Quartzites with the Addition of Converter Sludge*

Specimen from charge	Max. grain size, mm	Composition of addition,† %: CaO	Composition of addition,† %: Fe_2O_3	Firing temp. °C	Density, g/cm³	Open porosity, %	Compressive strength, N/mm²	Additional growth at 1450°C, %	Thermal expansion at 750°C, %	Temp. of the start of deformation under a load of 0.2 N/mm², °C
I	3	2	0,8	1400	2,34	22,2—22,8	33—44	0—0,1	1,34	1650
				1450	2,34	22,5—23,5	29—35	0—0,1	1,32	1660
II	3	4	1,0	1400	2,37—2,39	19,7—20,2	27—45	0,4—0,6	1,28	1660
				1450	2,35	21,9—22,3	37—38	0—0,1	1,12	1660
III	1	4	1,0	1400	2,35—2,36	21,1—21,4	56—58	0,1	1,18	1660
				1450	2,34	21,6—21,8	46—56	0,1	1,07	1670

*Refractoriness of all of the specimens 1690°C.
†0.8% of sodium lignosulfonate was added to all of the specimens.

TABLE 2. Mineral Composition and Tridymite Crystal Dimensions of Specimens from Pervouralsk Quartzites with the Addition of Converter Sludge

Specimen from charge	Firing temp., °C	Mineral comp., %: quartz	tridymite	cristobalite	glassy phase	Tridymite crystal size, μm: maximum	predominant
I	1400	10—15	35—40	35—40	10—15	60	25—30
	1450	5—10	45—50	35—40	5—10	110	30—70
II	1400	1—5	35—39	45—50	10—15	110	30—80
	1450	⩽1	54—55	35—40	5—10	110	30—70
III	1400	3—5	45—50	35—40	10—12	100	25—60
	1450	⩽1	61—65	30—35	3—5	130	35—90

An increase in firing temperature had a positive influence on the reduction in residual quartz in the dinas and the increase in the share of tridymite, especially in specimens from charge III, which is the result of its greater homogeneity with uniform distribution of the minealizing additions. The highest tridymite content (61-65%) and the lowest thermal expansion were found in specimens from charge III after firing at 1450°C, which indicates the possibility of solution of the problem of production of dinas from mixtures with a grain size of not more than 2 and 1 mm with high-production rod mills in the plants. With the use of such mixture a reduction in apparent density of the green use of such mixtures a reduction in apparent density of the green part after pressing is compulsory to prevent the appearance of overpressing cracks.

A more active form of iron oxide, iron scale in an addition composition of 4% CaO+1% FeO, was added to the dinas specimens from Ovruch quartzites. Laboratory specimens and parts of normal dimensions were pressed under a pressure of 80 N/mm². With a mixture moisture content of about 5.2% (grain size ≤ 3 mm) the apparent density of the green part reached 2.29-2.30 g/cm³. After drying the green part was fired with a final temperature of 1420°C with a hold of 50 h and at 1450°C with a hold of 12 h. The physicoceramic properties and mineral composition of the dinas specimens are given in Table 3.

As with use of Pervouralsk quartzites, an increase in firing temperature to 1450°C caused an improvement in the physicoceramic properties and structure of the dinas specimens with a reduction in residual quartz content and an increase in the share of tridymite.

The positive results in addition of scale to Ovruch quartzites served as the basis for a full-scale test of production of dinas parts for coke ovens at Krasnoarmeisk Dinas Plant. The question arose of the practical possibility of griding of the scale on the existing equipment of the plant's crushing and grinding department. The test of the grinding of the scale in the lime-iron slip production line did not provide positive results. Grinding of the scale in a short ball mill was insufficient. In the lime-iron slip the content of the coarser than 0.5 mm fraction varied within limits of 19-45% instead of the plants's standard content of the coarser than 0.09 fraction of not more than 10%.

TABLE 3. Characteristics of Dinas Specimens of Ovruch Quartzites with the Addition of Iron Scale

Firing temp., °C	Density, g/cm³	Apparent density, g/cm³	Open porosity, %	Compressive strength, N/mm²	Additional growth at 1450°C, %	Temp. of the start of deformation under a load of 0.2 N/mm², °C	Mineral composition, %			
							quartz	tridymite	cristobalite	glassy phase
1420	2,35	1,93—1,94	17,6—17,8	110—115	0,1	1650	9	46	30	15
1450	2,34—2,35	1,87	20,0—20,3	43,6—43,9	0—0,1	1650	⩽1	40—45	33—38	18—23

TABLE 4. Characteristics of Production Dinas Parts in Relation to the Method of Addition of the Scale*

Density, g/cm³	Open porosity, %	Compressive strength, N/mm²	Additional growth at 1450°C, %	Temp. of start of deformation under a load of 0.2N/mm², °C	Content, %		
					SiO_2	CaO	Fe_2O_3
With addition of the scale to the lime-iron mixture							
2,35—2,37	19,6—20,5	51—66	0,17—0,35	1630—1640	94,2—94,6	2,4—2,8	1,35—1,48
With addition of the scale by combined grinding with the quartz							
2,34—2,35	18,9—22,8	35—83	0,08—0,17	1630—1640	93,8—94,6	2,6—2,8	1,5—1,8

*The mineral composition of the parts with addition of the scale by combined grinding with the quartz was 7-15% quartz, 45-50% tridymite, 30-35% cristobalite, and 10% glassy phase.

In production of the first experimental lot of dinas parts the scale was ground in the experimental plant of Ukrainian Scientific-Research Institute for Refractories and added to the lime-iron mixture in its production line, as normally, with the milk of lime and the addition of sodium lignosulfonate solution. The mixture was transferred from the delivery mixer to the pressing and forming area. Ninety to a hundred tons of raw parts of different sizes, including about 20 tons of types 6196 (wall brick), 13324 (header brick), and 33343 (conduit brick) with weights of 6.1 to 14.65 kg, were pressed.

The mixture was prepared in mills and centrifugal mixers. The mixture contained not more than 3% of the coarser than 3 mm fraction and 48-50% of the finer than 0.5 mm, including about 27-28% of the finer than 0.09 mm. The moisture content of the mixture varied within limits of 5.2-6.0%.

The wall and header parts were pressed on toggler presses and the duct parts on a friction press. The parts were pressed to an apparent density of 2.24-2.26 g/cm³. After drying the parts were fired in a 243-m tunnel kiln with 10 pushes of the cars per day using the normal plant temperature cycle with a hold time at positions No. 34-52 of 45 h, including 18 h at 1415-1420°C.

After drying, the parts were inspected to Industry Standard 14-41-78. Inspection showed that for the wall and header parts the total scrap was 9-12%, including about 2.5% as the result of firing.

The dinas specimens with the addition of scale to the lime—iron mixture are characterized by uniform porosity and an increased compressive strength (Table 4).

Since grinding of the scale in the lime-iron mixture production line did not provide the standard content of coarser than 0.09 mm fraction, grinding of it together with the quartzite in a tube mill was tested. Such a variation was of interest for easing working conditions in preparation of the lime-iron mixture.

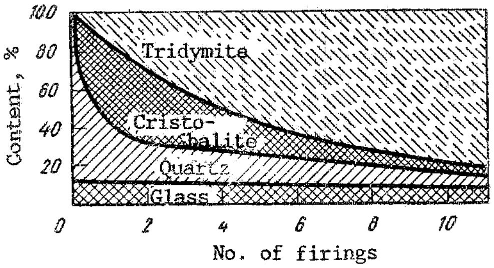

Fig. 4. Change in mineral composition of dinas refractories during firing.

Quartzite with a grain size of 5-10 mm and scale with a coarser than 0.5 mm content of about 30% were charged into the tube mill. With a grinder capacity of about 1.6 tons/h the content of coarser than 0.09 mm fraction in the mixture did not exceed 9.2% and the density of the mixture varied within limits of 2.65-2.84 g/cm^3,* satisfying the requirements of the production instructions not only for coarser than 0.09 mm fraction content but also for addition of iron oxide to the dinas (0.6-1.0%).

Combined grinding of quartzite with scale in a tube mill did not require installation of additional equipment and had a positive influence on homogeneization of the charge. Elimination of the iron addition from the lime-rion mixture has a favorable influence on reducing the density of the slip and increasing its activity.

In production of the second experimental lot a finely ground mixture of quartzite with scale was added to the ground quartzite and the milk of lime together with the additions of sodium lignosulfonate solution were supplied to the mixers. The alkalinity and moisture content of the mixtures met the standards of the technical instruction in effect in the plant. The parts for coke ovens were pressed on friction presses and the type D9, D5, and DM-20 parts on turret presses. The mixtures contained not more than 1% of the coarser than 3 mm fraction and 54-56% of the finer than 0.5 mm, including about 31-33% of the finer than 0.09 mm. After drying, the parts were fired in a 243-m tunnel kiln with 11 pushes of the car per day. In positions Nos. 31-52 the temperature varied from 1400 to 1420°C and the hold at 1415-1420°C did not exceed 22 h.

The physicoceramic properties of the parts are given in Table 4. With the addition of scale in the dry condition in combined grinding with quartz (≤ 0.09 mm) with a dinas specimen density of 2.34-2.35 g/cm^3 the residual quartz content in them dropped to 7-10% while the share of tridymite increased to 45-50%. The physicoceramic properties of the dinas parts completely met specification requirements.

A subsequent reduction in residual quartz in the dinas and an increase in the share of tridymite is possible only by increasing the temperature in the hold, as was noted above, since by itself an increase in hold time does not lead to the desired results. A a confirmation of this Fig. 4 shows the change in mineral composition of dinas parts after 11 successive firing [9, p. 274].

The positive results obtained on increasing the quality of dinas parts served as the basis solution of the question of setting up of adding of the scale to the tube mill and switching production to the new method, including a finer grain size distribution of the mixtures and the addition in place of pyrite roasting residues of scale in the dry condition in the form of combined grinding with quartzite.

In the first months of operation of the plant with the new method the density of the lime water was increased to 1.3 g/cm^3 and the activity after addition of 0.7% sodium lignosulfonate solution increased to 30% with respect to CaO. The removal from the lime-iron mixture of iron oxides significantly improved working conditions in the area for preparation of the milk of lime and increased the strength of the green part after drying.

*Determined by the rapid method described in Ogneupory, No. 3, 131-133 (1948).

CONCLUSIONS

Replacement of pyrite-roasting residues with scale is a measure improving the physicoceramic properties and structure of dinas parts for coke ovens. The addition of scale in the dry condition makes it possible to prepare the milk of lime without iron oxides, increasing its activity for strengthening the raw part after drying.

Addition of scale with the active form of iron oxide FeO promotes a reduction in parts in the residual quartz content and an increase in the share of tridymite to 45-50% instead of the 30-35% with addition of pyrite-roasting residues in firing of dinas in tunnel kilns. A further improvement in the structure of dinas with an increase in the share of tridymite to 55-60% and more is possible only after increasing the final temperature of the hold to 1440-1450°C in firing parts from Ovruch quartzites. The year and a half of positive experince of Krasnoarmeisk Dinas Plant in the addition of scale to dinas parts for coke ovens should be extended to Krasnogorovka and Pervouralsk Plants.

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