RAW MATERIALS

EFFECT OF CHROMIUM AND ZIRCONIUM OXIDES ON PROPERTIES OF BOBROVSK DEPOSIT QUARTZITE RAMMING MIXES

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Processing research is carried out on Bobrovsk deposit quartzites. The effect of chromium and zirconium oxides, aluminochromium catalyst waste, and baddeleyite-corundum object scrap, on sintering, structure formation, and properties of ramming mixes is studied. Laboratory tests are performed for slag resistance.

Keywords: quartzite, ramming mix, induction furnace lining, refractories, sintering, slag resistance.

Previous research has established that the mineral composition of Bobrovsk deposit quartzite is almost pure entirely crystalline cemented quartzites of two types, i.e., light and dark [1, 2]. In a practical respect both varieties are equivalent and contain 98.82 and 98.06 wt.% SiO_2 respectively. Grain size and substance composition of ramming mixes for lining ferrous and nonferrous metallurgy induction furnaces have been developed on the basis of Bobrovsk deposit quartzite.

A feature of induction furnaces is the small lining thickness. However, the smaller the "crucible" wall thickness, the shorter its service life, and there is also a reduction in furnace operating reliability. Therefore improvement in chemical and corrosion resistance of an inductor lining is an important task. Production studies were carried out for the possibility of improving lining corrosion resistance for a ramming induction mix based on Bobrovsk deposit quartzite.

In preparing an induction mix the most widespread sintering addition is boron oxide (boric acid). A study of the effect of B_2O_3 on mix properties of Bobrovsk quartzite has shown that addition in an amount of 1.5 – 3.0 wt.% is adequate for forming a dense and strong structure of a ceramic "crucible". It is well known [3] that a melt based on boron oxide does not facilitate quartzite degeneration from one polymorphic modification to another, but it effectively sinters quartzite materials. Proceeding from theoretical assumptions it is considered possible to improve corrosion resistance of refractory materials with respect to slag, or any other corrosive factor [4]:

– by increasing chemical (thermodynamic) material strength;

– by increasing thermal shock resistance (resistance to drops in temperature);

– by reducing reaction surface between material and melt (reducing pore volume and size);

– by changing the boundary wetting angle between material and melt.

With respect to quartzite mixes and ferrous metallurgy molten slags the most effective industrial method of improving corrosion resistance is a change in thermal shock resistance and material wettability with slags. This is achieved by introducing into a charge composition subordinate amounts of substances not reducing material refractoriness and strength, but improving its other properties.

Of materials known currently, not wetted by melts based on iron, the most abundant, and consequently cheap and accessible, are materials based chromium and zirconium oxides.

With respect of value of Gibbs energy Cr_2O_3 and ZrO_2 are thermodynamically stable [5], and the oxide heat of formation is 1141.32 and 1101.30 kJ/mole respectively. This is much greater than similar values for FeO and MnO (265.02 and 385.35 kJ/mole respectively), i.e., the main components of steel oxidation at high temperature. Trivalent iron and manganese oxides also have lower values of heat of formation (822.71 and 958.36 kJ/mole respectively), than Cr_2O_3 and ZrO_2.

Chromium does not form chemical compounds or solid solutions with SiO_2. In the binary system Cr_2O_3–SiO_2 there

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is an extensive region of two immiscible melts at a temperature above 2200°C [6], which is maintained with introduction of other components. Zirconium dioxide forms a chemical compound $ZrSiO_4$ with SiO_2, and formation of a eutectic melt in a pseudobinary system $ZrSiO_4$–SiO_2 is possible at a temperature of about 1650°C [6], above which zircon $ZrSiO_4$ breaks down again into ZrO_2 and SiO_2. Taking account of this Cr_2O_3 is more preferable as an oxide maintaining stable properties up to higher temperatures [4]. From a physicochemical point of view chromium oxide is also a stable compound since it forms solid solutions with sesquioxides of iron, manganese, and aluminum whose synthesis proceeds rapidly since the ionic radii of chromium (III), aluminum (III), and manganese (III) correspond to the first Goldschmidt rule, i.e., they differ from each other by not more than $10 - 15\%$ [7, 8]. A significant liquation region in the system Cr_2O_3–SiO_2 and low solubility of chromium oxide in SiO_2 in a high silica melt gives rise to limited melt penetration into an object and increased system corrosion resistance.

TEST PROCEDURE

Materials used. In the course of work the following were used: Bobrovsk deposit quartzite fractions $3 - 1$, $1 - 0$, and <0.063 mm (TU 1528-004-94779610–2009); aluminochromium catalyst for gas cleaning from sulfur IP-21; baddeleyite-corundum object scrap, 25.0 wt.% ZrO_2; commercial grade zirconium oxide (TU 6-09-27-180–88); commercial grade chromium (III) oxide (GOST 2912); commercial grade B boric acid (GOST 18704); commercial grade lignosulfonate (TU 2455-028-00279580–2004).

Research methods. The apparent density and open porosity of refractory objects was determined according to GOST 2409. Ultimate strength in compression was determined according to GOST 4071.1, and slag resistance according to DIN 51069, part 2 (crucible method).

Mix preparation and specimen manufacture. Mixes were prepared in a laboratory planetary mill. Specimens in the form of cylinders 50 mm in diameter and height, and "crucible" specimens with height and diameter of 55 mm with an opening 25 mm deep and in diameter, were manufactured by one-sided semidry compaction in a laboratory hydraulic press under a pressure of 145 MPa, and this corresponds to pneumatic tamping conditions. Specimens for determining strength in compression were fired in a laboratory electric furnace with chromite-lanthanum heaters at 1600°C. An identical amount of metallurgical slag was placed in a "crucible" specimen and heated to 1600°C.

Test compositions. The basic quartzite "crucible" ramming mix based on Bobrovsk deposit quartzite recommended for application previously was adopted. The grain size composition of charges is presented below:

Fraction, mm. . . . . . $3 - 1$ $1.0 - 0.5$ $0.5 - 0.088$ <0.088
Content, wt.% 30 20 25 25

Boric acid at 1.5 wt.% and 4 wt.% temporary binder (CLS) were added to a charge. In the course of operation additives improving corrosion resistance were added to a mix. Test mix compositions are presented in Table 1.

TEST RESULTS

Physicochemical properties of specimens after heat treatment are presented in Table 2. Action of the additives appears to be different. The effect of almost all additives on the amount of open porosity is almost identical. Mix 1 of control composition after firing at 1600°C had open porosity of 26%, and the rest of the mixes, apart from 2, had the same amount of open porosity. Some lower open porosity (23%) was typical for mixes 2 and 4, which contained commercial grade chromium (III) oxide as an additive.

Introduction into the composition of charge mixes 2 and 4 of chromium oxide in an amount of 5 and 10 wt.% respectively promoted an increase in apparent density of specimens to 2.07 and 2.1 g/cm^3 (see Table 2). It should be noted that there are compositions of greater density, for example composition 6, and this density is not achieved as a result of charge compaction, but due to the greater density of the addi-

TABLE 1. Properties of Test Mixes $(1 - 9)$*

Charge fraction, mm	Component content in test mix charge								
	1	2	3	4	5	6	7	8	9
$3 - 1$	Qu	Qu	Qu	Qu	Qu	Qu	Qu	Qu	Qu
$1.0 - 0.5$	Qu	Qu	Qu	Qu	Qu	Qu	Qu+Bc 10 %	Qu	Qu
$0.5 - 0.088$	Qu	Qu	Qu	Qu	Qu + Bc 5%	Qu + Bc 10%	Qu	Qu	Qu
<0.088	Qu	Qu + C 5%	Qu + Cc 5%	Qu + C 10%	Qu	Qu	Qu	Qu + Z 5%	Qu + Z 10%

* Qu is Bobrov formation quartzite; C is commercial chromium oxide; Cc is aluminochromium catalyst waste; Bc is baddeleyite-corundum object scrap; Z is commercial zirconium oxide.
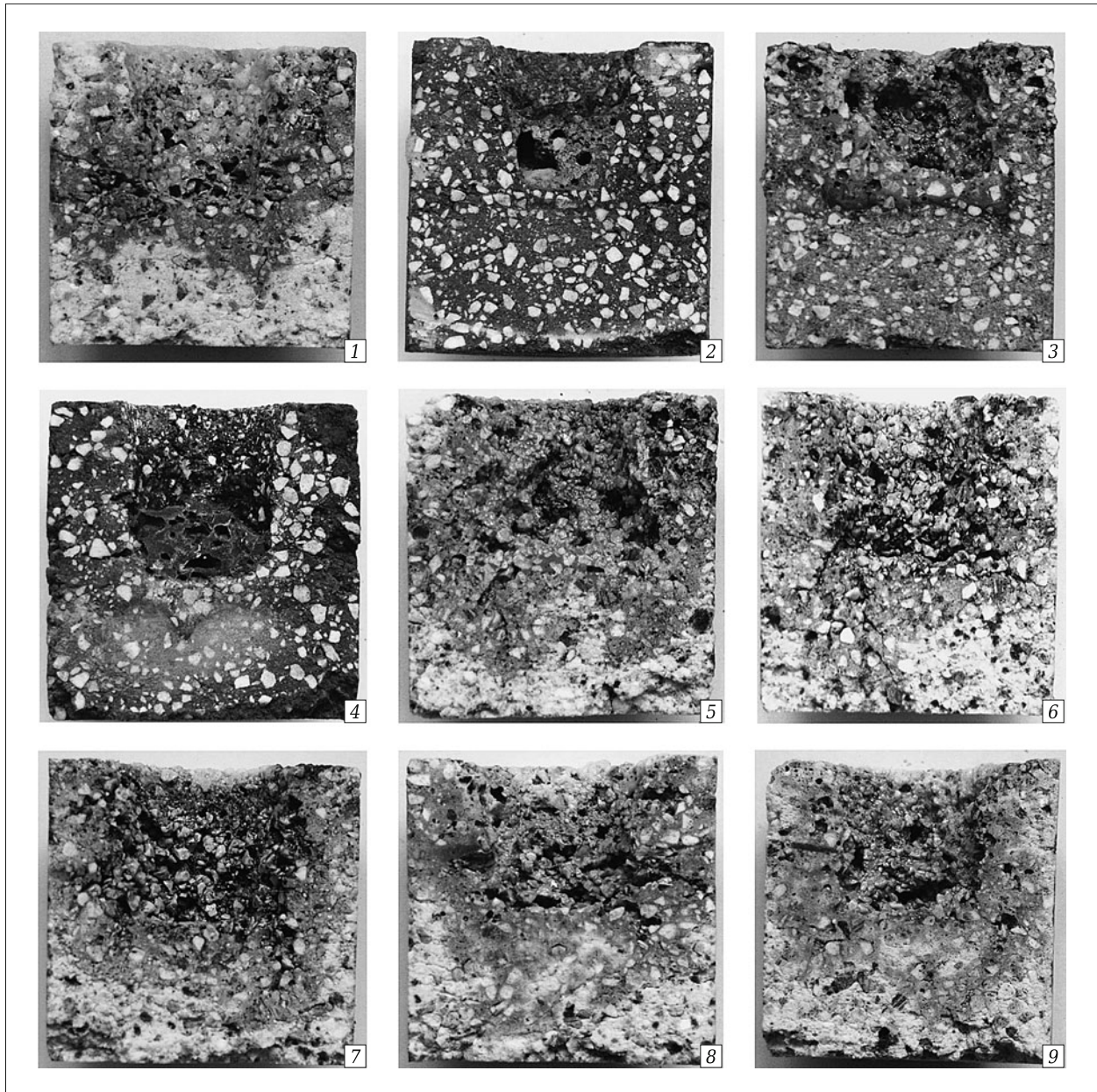
Fig. 1. Specimens 1 – 9 of test mixes (shown in platens) after slag resistance testing.

TABLE 2. Test Mix Specimen Physicochemical Property Indices

Weight (see Table 1)	Water absorption, %	Open porosity, %	Apparent density, g/cm³	Ultimate strength in compression, MPa
1	13	26	1.96	10
2	11	23	2.07	16
3	14	26	1.96	13
4	11	23	2.1	16
5	13	26	2.01	12
6	13	25	2.11	17
7	13	26	2.03	9
8	13	26	2.0	12
9	12	25	2.08	10

tive, i.e., baddeleyite-corundum object scrap, since its density is markedly higher than that of chromium oxide due to presence within it of zirconium dioxide, whose density is 6.0 g/cm³.

Ultimate strength in compression σ_{co} for specimens of mixes 2 and 4 (see Table 2) is 16 MPa, which is markedly above the σ_{co} for mix 1 (10 MPa). Only a specimen of mix 6 has an ultimate strength of 17 MPa, i.e., approximately the same as that for compositions using chromium oxide. Ultimate strength in compression is characterized by material structure after firing and reflects the nature of the bond between charge grains. This is especially marked for specimens 6 and 7, which contain an identical additive of 10%

baddeleyite-corundum object scrap, but different fineness. In mix 6 the additive was fraction 0.5 – 0.88 mm, and for mix 7 it was 0.5 – 1.0 mm, i.e., coarser. The ultimate strength of mixes 6 and 7 is 17 and 9 MPa respectively. This indicates that additives, as recommended in technical standard documents, should be introduced in the form grains not coarser than 60 μm. Commercial grade chromium (III) oxide used in a the work is a very fine material, whose grain size is mainly less than 2 μm. Introduction of commercial grade zirconium dioxide (mixes 8 and 9) and chromium-containing catalyst (mix 3) did not have a marked effect on increasing ultimate strength in compression, and the σ_{co} for specimens of these mixes is at the level of the control mix index. Results of studying slag resistance are presented in Fig. 1 and in Table 3.

Results of petrographic studies show that the most resistant to molten slag are specimens of mixes 2 and 4, which after testing were not impregnated and not attacked by slag (see Table 3), whereas control specimen 1 under similar conditions had an impregnation area of 12.4 cm^2 and attack of 4.7 cm^2. Connected with these indices is the depth of "crucible" impregnation with slag; for control specimen 1 it was 10 – 15 mm with dissolution of material to a depth of 5 – 7 mm, whereas for specimens of mixes 2 and 4 surface melted layer thickness was not more than 1 mm. Absence of impregnation by slag was reflected favorably in the structure of crucible material; for the melting area (thickness ~1 mm) it remained unchanged and all of the indices were held at the original level.

The rest of the mixes in contact with slag showed about the same results. Dissolution in slag was observed at first for

TABLE 3. Results of Slag Resistance Determination

Mix	Area, cm^2		Nature of attack
	impregnation	attack	
1	12.4	4.7	Deep specimen impregnation (10 – 15 mm) with partial matrix dissolution to a depth of 5 – 7 mm. Coarse grains fuzed and partly washed out from specimen structure. Specimen structure after testing loose with shrinkage cracks.
2	0	0	No specimen impregnation, at "crucible" inner surface there is a thin transitional fuzed layer. All slag remained in "crucible". Partial attack of the "crucible" surface (up to 1 mm) at the slag–refractory–air boundary (in the slag boiling area). Lower part of "crucible" unchanged. Specimen structure uniform, dense, almost unchanged.
3	10.6	9.2	Deep specimen impregnation over whole contact area (10 – 15 mm), and also attack of "crucible" working surface to a greater depth (5 – 8 mm) both for matrix, and for grains. Melting out of coarse grains from specimen structure, and trickling of them to "crucible" bottom. Unchanged area uniform, dense, with individual microcracks.
4	0.3	0.4	No specimen impregnation, "crucible" inner surface has thin (up to 0.1 mm) transitional fuzed layer, not entirely covering "crucible" surface. Almost all slag remained in "crucible". Attack of "crucible" surface up to 1 – 3 mm through matrix is observed at three-phase slag–refractory–air boundary in area of slag boiling. Specimen structure uniform, dense, almost unchanged after slag melting. No marked quartzite grain degeneration observed.
5	10.4	3.4	Specimen impregnation over almost whole "crucible" depth (up to 25 mm) over all contact surface with slag. Attack of "crucible" walls over all contact surface through specimen matrix. Coarse grains at "crucible" surface partly washed out of structure. Loose, microcracked specimen structure in contact area.
6	9.7	4.2	Specimen impregnation over almost the whole "crucible" depth (up to 15 mm) over all contact surface with slag. Attack of "crucible" walls at molten slag level through both specimen matrix, and granular surface to a depth of 5 mm. Coarse grains at "crucible" surface partly washed out from structure and fuzed. Loose, microcracked specimen structure in contact area.
7	10.2	4.3	Specimen impregnation up to depth of 10 mm over whole contact surface with slag. Attack of "crucible" walls at the molten slag level both through matrix, and through granular part up to a depth of 5 mm. Coarse grains at "crucible" surface partly washed out from structure and fuzed. In impregnation area specimen structure loose, microcracked.
8	9.1	2.4	Specimen impregnation over whole contact area to a depth up to 15 mm, and also attack of "crucible" working surface at the slag boiling level to a depth of 4 – 7 mm both through matrix, and partly though grains. Specimen dense in impregnation area, no cracks, impregnation occurred through matrix.
9	8.5	2.3	Specimen impregnation over whole "crucible" contact area to depth up to 8 – 12 mm, and also attack of "crucible" working surface at the slag boiling level up to a depth of 3 – 5 mm both through matrix, and partly through grains. Most changed layer at "crucible" surface porous, with traces of melt boiling. Impregnated layer dense, firm, no cracks.

the fine part of a charge, and then the coarse quartzite fraction, and the depth of dissolution varies from 4 – 7 (for mix 8) to 8 – 12 mm (for mix 9).

CONCLUSION

With the aim of improving corrosion resistance for quartzite mixes for lining induction furnaces against the action of slag, charge alloying was carried out with chromium, zirconium oxides, and secondary materials, containing these oxides.

The optimum additive of those in question is chromium (III) oxide. The optimum concentration in a charge should be considered as 3.5% (mix 2) with the following content of components, wt.%: quartzite faction 3 – 1 mm 30, 1.0 – 0.5 20, 0.5 – 0.088 mm 25, <0.088 mm 20, chromium oxide 3 – 5. A further increase in chromium oxide concentration in a charge does not provide a marked improvement in physicochemical properties or improvement in slag resistance (see Table 2).

Introduction of chromium oxide into a quartzite charge facilitates an increase in strength. The σ_{co} for a specimens of control mix 1 is 10 MPa, for mix with addition of 5% Cr_2O_3 it is 16 MPa, and this undoubtedly promotes a change in binder composition (glassy phase in material) in specimens, whose strength properties on cooling objects are not reduced, and conversely they increase.

Open porosity of specimens of all test mixes is about the same (23 – 26%), and this points to the similarity of their structures. This has been noted previously by other researchers and is connected with quartzite polymorphism, whose loosening of grains levels out an increase in the amount of open porosity for all mixes.

Addition of chromium oxide should desirably be made as a fine-grained component (.088 mm), since this quartzite fraction has the greatest dissolution rate in slag; the addition should be mixed (distributed) carefully both through the volume of the fine part, and throughout a charge as a whole.

Coarsening of an additive, as has been shown in specimens of mixes 6 and 7, is undesirable, since there is a reduction in ultimate strength in compression with an increase in material reaction rate with slag.

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