EFFECT OF COMPOSITION OF GRAPHITE-CONTAINING CRUCIBLE AND MUFFLE MASSES ON STRUCTURE OF SAMPLES BASED THEREON

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Introduction

The first items of information about metal melting in crucibles proceed from Aristotel, but one can speak about the manufacture of crucibles only since the XVI century, when making of metals in crucibles has reached relatively large volumes and natural graphite was started to be used, which in a mix with clay has allowed to produce stable crucibles [1]. Last decades the role of graphite/carbon in the manufacture of crucibles for smelting of non-ferrous metals and steels, foundry ladles for teeming steel, lining for oxygen blow furnaces for melting steels, magnesite- and alumina-carbon bricks and other purposes steadily grew [2]. It was connected with intensification of known and creation of new processes of smelting and pouring of non-ferrous metals and alloys, special steels and techniques of their processing (secondary processing in steel-pouring or intermediate ladles and others) using a graphite(carbon)-containing refractories, for only they have the most high thermal resistance among all kinds of refractories [3,4]. The disadvantage of these refractories is that oxidation of graphite begins at temperatures over 500 ^{o}C and decrease of which influences efficient and safety smeltings and reliability of operation of articles made of such refractories [5].

A number of the authors [6] have shown that at low temperatures oxidation of graphite is determined by its reactivity, and at elevated ones diffusion of oxygen becomes decisive. The reduction of permeability and size of opened pores, as well as the specific surface area by BET (S_w), decreases the speed of oxygen diffusion and, hence, speed of graphite oxidization, increasing service life of such refractories.

It is the analysis of parameters of pore structure of graphite-containing refractories by an example of crucible and muffle masses of half-dry moulding that the present report is devoted to.

Experimerntal

From each specified mass of 8÷15 % humidity, the structure of which is presented in Table 1, 3 laboratory samples (∅ 36 *mm*, H 10-14 *mm*) were molded (P_m = 25 *MPa*) for study the pore structure. On each sample apparent (ρ_a) and pycnometric (ρ_p: by *isooctane* [7] and He - using *Auto-Pycnometer-1320* of "Micromeritics", USA) densities, opened porosity (P_o) as well as gas permeability (K_g) by a modified technique "flow in vacuum" [8], the essence of which consists in measurement of air inleakage speed into a preevacuated vessel of known capacity separated from the atmosphere by the investigated material sample of known sizes, were determined.

Table 1
Composition of crucible and muffle masses (*wt.* %)

Code of sample	Additive	Graphite	Clay	Antioxidizer	SiC	Humidifier-binder,↑100 %
Б*	-	49	38	10	3	water,10
В*	-	49	38	10	3	clay slip,15
Т**	-	49	38	10	3	SS,10
Г*	frit,5	49	33	10	3	SS,10
Д*	CaF_2, 0.9	54.4	35.6	5.7	3.4	SS,10
Е*	CaF_2, 0.9	54.4	35.6	5.7	3.4	clay slip,15
І*	B_2O_3,5.0 +CaF_2, 2.0	49	36	5	3	SS,10
М**	-	21.5	49	9.5	20	SS,10

* Heat Treatment at 1350 ^{o}C with isothermal exposure 4 *h*;
** HT at 900 (T-1; M-1), 1100, 1400 and 1600 ^{o}C (T-4; M-4)

On a sample with average values of these indices the value of S_w (by Kr and N_2, *AccuSorb 2100 E*) and the character of distribution of pore specific volume (V, cm^3/g) in terms of the sizes of their equivalent radii (R_{eq}: *AutoPore 9200*) as well as the pore volume share (ΔV) falling on *capillary* pores by which large *bottle-shaped* pores are connected therebetween and with the sample external surface, were determined. The characteristics of the investigated samples are presented in Table 2.

Results and Discussion

As follows from the analysis of influence of a type of a humidifier-binder on the pore structure (samples В2, Б2 and Т-3), the most dense (minimum values of V and K_g) structure is formed by silicate sol (SS), that is also observed on the samples Д2 and Е1 with the low-melting additive CaF_2.

As to the additives, from all the investigated ones only frit results in formation of the fineporous refractory (R_{max} = 0.18 μm) with low K_g and S_w. The additives CaF_2 and B_2O_3, removed at burning, create coarse-porous material (R_{max} = 2.2÷3.1 μm) with high permeabi-

lity (samples Д, E, and I).
Influence of the heat treatment temperature (HTT) was analyzed on the samples of crucible (code T) and muffle (M) masses. It is found, that the nonbaked material (T-0) is characterised by a peculiar finepore structure, in which 50 % of opened porosity are *Knudsen's* pores (R_{eq} < 35 *nm* [9]). Baking at 900 ^{o}C results in decrease of the *Knudsen's* pores (V_{kn}) volume and growth of *transitional* pores (35 *nm* <R_{eq} <3.5 *μm* [9]) volume at the expense of removal of physically bound moisture and reorganization of the refractory clay structure.

Further growth of HTT leads to the material shrinkage, attaining the maximum at 1400 ^{o}C and accompanied by decrease of the V_{kn} and V_{tr} pores share (in the interval of R_{eq}=35 *nm* ÷ 0.35 *μm*) in the total volume of open porosity. These changes are also reflected in change of the values K_g and S_w, as between S_w and V_{kn} a direct correlation (r = 0.9; n = 15) exists. The HT at 1600 ^{o}C results in evaporation of a part of Si crystal, used in the mixture as an antioxidizer (mass losses of T-4 samples as compared to T-0 and T-1 were Δm = 37 and 23 %, respectively), as well as in an irreversible thermal expansion caused by cracking according to Mrozowski [4,6]. This sharply increases the volume V_{tr} and forms in the refractory structure *Poiseuille's* pores (R_{eq}>3.5 *μm*), the volume of which makes up more than 1/4 of the refractory opened porosity. Practically the same picture is also observed for samples from the muffle mass with the only difference, that in the heat-treated at 1600 ^{o}C material (Δm=15 % as compared to M-1 samples) the half of open porosity are *macropores* with R_{eq}>10 *μm*. Their formation is explained, apparently, by a lower content of graphite in the mass, that sharply reduces probability of its reaction with evaporated Si and formation SiC.

Conclusion

The most dense graphite-containing refractories on the basis of crucible and muffle masses with low values of P_o, K_g and S_w and, hense, the most reaction-resistance, were obtained at baking temperatures of 1100-1400 ^{o}C with silicate sol as a binder.The introduction of the low-melting additives leads to growth of the size of prevailling pores, thereby increasing K_g and S_w of the refractories. The heat treatment (exploitation) of the refractory products of such structure at the temperature of 1600 ^{o}C is undesirable, as it sharply increases the sizes and volume of open pores in the materials.

References

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Table 2 - Characteristics of pore structure of samples of refractories

Code of sample	By isooctane			Density, g/cm^3		V, cm^3/g	ΔV, cm^3/g	R_{max}, *μm*	S_w, m^2/g	K_g, cm^2/s
	ρ_a, g/cm^3	ρ_p, g/cm^3	P_o, %	by Hg	by He					
Б2	1.881	2.350	19.97	1.863	2.371	0.1300	0.0417	0.63	0.62	0.0205
В2	1.829	2.362	22.55	1.827	2.386	0.1434	0.0475	0.89	0.98	0.186
T-0-1	1.955	2.404	18.67	1.945	-	0.1033	0.0634	0.03	14.74	0.0044
T-1-2	1.950	2.414	19.21	1.935	2.443	0.1068	0.0616	0.05	2.90	0.0084
T-2-2	2.029	2.376	14.62	1.997	2.383	0.0849	0.0408	0.43	0.98	0.0058
T-3-1	1.992	2.365	15.74	-	2.360	0.0450	-	0.40	0.65	0.0058
T-4-1	1.499	2.715	44.79	1.483	2.733	0.2365	0.0636	2.82	3.25	1.82
Г2	2.044	2.352	13.08	2.033	2.279	0.0848	0.0128	0.18	0.55	0.0046
Д2	1.708	2.397	28.74	1.708	2.385	0.1672	0.0739	2.18	0.84	0.334
Е1	1.710	2.435	29.75	1.706	2.417	0.1842	0.0881	2.18	-	0.333
И1	1.569	-	-	1.723	2.297	0.1614	0.0312	2.52	0.91	0.0253
M-1-2	1.997	2.603	23.27	1.991	2.656	0.1175	0.0689	0.05	5.82	0.0104
M-2-2	2.081	2.557	18.63	2.064	2.580	0.0943	0.0398	0.56	0.92	0.0146
M-3-3	2.154	2.519	14.49	2.149	2.549	0.0846	0.0190	0.63	0.34	0.011
M-4-1	1.680	2.802	40.05	1.752	2.804	0.2267	0.0759	15.86	0.42	16.9