PHOSPHATE BINDERS IN REFRACTORIES FOR STEELCASTING

G. É. Solovushkova, S. P. Shmitt-Fogelevich,
G. G. Mel'nikova, L. I. Romanenko,
L. G. Stochek, and B. G. Markelov

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In a joint project with the Novomoskovsk Chamotte Plant (NCP) the All-Union Institute of Refractories has developed a technology for the production of alumina — graphite nozzles for uphill casting on continuous-casting equipment [1, 2]. The principal components of the batch for the nozzles are high-alumina chamotte, graphite, clay, and synthetic corundum. The binder used, in addition to the clay, is aluminophosphate $Al_2O_3 \cdot 3P_2O_5$ (dry composition) added in the proportion of 10 wt. % on 100 wt. % dry components.

The chief merit of this technology for the production of alumina — graphite refractories with an aluminophosphate binder (APB) is the fact that it permits low-temperature firing (650°C). This is very important for graphite-containing products because it eliminates the need for costly precautionary measures to prevent the burn-out of the graphite.

The use of APB for concretes of various types, is of course, a well-known fact. For refractories intended for a service at the steelcasting temperature (1560°C) this binder has been used only in one case. Nozzles with APB have been in use in the continuous-steelcasting (CSC) equipment of the Novolipetsk Metallurgical Plant (NMP) for several years. The experience gained during that period by the maker and user of the nozzles makes it possible to advance the following main conclusions about their quality.

1. The strength is inadequate for intricate-shape nozzles, more particularly for nozzles with a bottom, but it is adequate for the manufacture of tubular nozzles which in the CSC of the NMP had a useful life of two to four melts, i.e., up to 300 tons steel.

2. With an APB prepared at the plant immediately prior to adding it to the batch, the molding properties of the latter were uneven so that the nozzle production process was unstable and the percent spoilage considerable.

3. There were cases when the nozzles broke into pieces after the first third or half of a melt.

These facts made it necessary to improve the quality of the nozzles. The work carried out in this respect provided for the retention of a phosphate binder.

TABLE 1. Characteristics of Aluminophosphate-Bonded Alumina—Graphite Nozzles before and after Use

Nozzle	P_2O_5 content, %	Open porosity, %
Unused	5,39	12,2
After three melts	1,96	26,3
After half a melt	0,58	32,4

All-Union Institute of Refractories. Novomoskovsk Chamotte Plant. Translated from Ogneupory, No. 11, pp. 48-53, November, 1975.

TABLE 2. The Properties of the Phosphate-Bonded Alumina–Graphite Specimens*

Binder	Firing temp., °C	Open porosity, %	Cold-crushing strength, kg/cm²
APB	650†	11,7	194
ACPB No. 1		12,3	244
ACPB No. 2		11,4	262
APB	1600	31,8	87
ACPB No. 1		27,0	184
ACPB No. 2		23,9	212

*Mean results for three to five specimens.
†Thermal strength before cracking two to four, to destruction over 25 temperature reversals 1300°C – water.

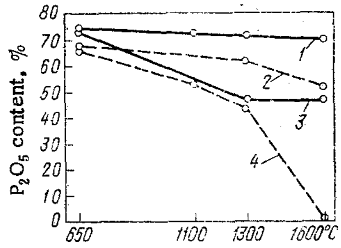

Fig. 1. The loss of P_2O_5 in APB (1, 2) and ACPB No. 1 (3, 4) in heat treatments in an oxidizing (——) and a slightly reducing (– – – –) medium.

It was found necessary to analyze the part played by the phosphate binder during molding and in the processes developing in the nozzle in service.

The instability of the molding properties of the batch proved to be attributable to the following causes. The APB was prepared by neutralizing orthophosphoric acid heated to 80°C with aluminum hydroxide. The reaction of these substances gives a mix of ortho-, meta-, and pyrophosphates of aluminum [3-6]. The adhesion properties of phosphates are temperature-dependent in addition to which some of the phosphates are converted to others which are equally temperature-dependent. These are the sources of the uneven properties of the batch.

The high-temperature state of an APB was analyzed in earlier research. It was shown [4] that at a temperature above 1000°C an aluminophosphate binder is fixed mainly as aluminum orthophosphate $AlPO_4$ in the cristobalite phase. At 1100-1550°C the cristobalite is dissociated and some of the P_2O_5 is volatilized, above 1550°C the dissociation of the bond ceases, and after holding at 1600°C the $AlPO_4$ is immobilized as a vitreous phase. Khoroshavin et al. defined a more precise temperature range (1460-1480°C) over which $AlPO_4$ is dissociated to Al_2O_3 and P_2O_5. With prolonged heating at 1600°C the dissociation of the bond ceases and the $AlPO_4$ is determined in the form of high-temperature cristobalite.

To judge by the cited published information, the service conditions of the nozzles on CSC plant are highly unfavorable for the APB. This assumption was checked by determining the open porosity and P_2O_5 content of unused nozzles, of nozzles used for three melts, and of nozzles which broke up after half a melt. The data in Table 1 suggest that the durability of the nozzles is directly related to the degree of dissociation of the bond.

Recent publications contain much information about aluminochromophosphate binders (ACPB) with better technical characteristics than APB [7-9].

In the investigation reported here tests were carried out with ACPB of two compositions: $Al_2O_3 \cdot 0.2\ Cr_2O_3 \cdot 3P_2O_5$ (No. 1) and $Al_2O_3 \cdot 0.8\ Cr_2O_3 \cdot 3P_2O_5$ (No. 2). Both binders were produced by the Moscow organization Énergotekhprom, i.e., No. 1 in accordance with Technical Specifications TU-34-4620-73 and No. 2 in accordance with an order from the All-Union Institute of Refractories and the NCP.

The quality of the binders was checked by molding specimens 40 mm in height and 38 mm in diameter from a batch used at the NCP for nozzles. The batch consisted of 60% high-alumina chamotte, 15% flake graphite, 15% clay grade DN1, and 10% synthetic corundum.

The binders used were APB and ACPB of compositions Nos. 1 and 2. The binders were added in the proportion of 6-10% on 100% dry components.* The specimens were fired twice, viz., at 650°C and again at 1600°C with 2 h holding. The results of an analysis of the specimens are set out in Table 2.

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*N. K. Arkhipova participated in the work.

TABLE 3. X-Ray Phase Analysis of the Heat-Treated Binders

Medium	Temp., °C	Aluminophosphate binder			Aluminochromophosphate binder No. 1		
		constituent phases	phase modification	measured interplanar spacing, Å	constituent phases	phase modification	measured interplanar spacing, Å[*]
Oxidizing	650	$Al(PO_3)_3$	A	4,42; 3,68; 3,45; 2,94; 2,70	Glass	—	Broad halo in the region of angles 6-20°
	1100	$Al(PO_3)_3$ $AlPO_4$	A Cristobalite	4,37; 3,68; 3,46; 2,94; 2,69 4,09; 3,16; 2,88; 2,51	$Al(PO_3)_3$ $Al(PO_3)_3$ $AlPO_4$	C A Cristobalite	3,82; 3,69; 3,37; 3,03; 2,75; 4,38; 3,69; 3,44; 2,95; 2,69 4,13; 3,20; 2,90; 2,52
	1300	$Al(PO_3)_3$ $AlPO_4$	A Cristobalite	4,42; 3,69; 3,48; 2,94; 2,69 4,13; 3,16; 2,88; 2,51	$Al(PO_3)_3$ $AlPO_4$	C Cristobalite	3,83; 3,65; 3,38; 3,02; 2,75 4,10; 3,16; 2,87; 2,51
	1600	Glass $AlPO_4$	— Cristobalite	Broad halo in the region of angles 6-20° 4,06	$AlPO_4$	Cristobalite	4,15; 3,17; 2,87; 2,51
Slightly reducing	650	$Al(PO_3)_3$ $AlPO_4$	A Cristobalite	4,39; 3,67; 3,42; 2,93; 2,69 4,08	Cristobalite	—	Broad halo in the region of angles 6-20°
	1100	$Al(PO_3)_3$ $Al PO_4$	A Cristobalite	4,34; 3,68; 3,45; 2,95; 2,70 4,08	$AlPO_4$ $Al(PO_3)_3$	Cristobalite C	4,10; 3,17; 2,87; 2,51 3,83; 3,36
	1300	$AlPO_4$	Cristobalite	4,09; 3,17; 2,87; 2,51	$AlPO_4$	Cristobalite	4,08; 3,16; 2,86; 2,50
	1600	$AlPO_4$ Glass	Cristobalite —	4,05; 3,14; 2,86; 2,49 Broad halo in the region of angles 6-20°	Solid soln. Al_2O_3—Cr_2O_3	—	3,55; 2,58; 2,40; 2,09 (3,47—3,62); (2,55—2,67); (2,37—2,47); (2,08—2,17)

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[*] In parentheses the corresponding interplanar spacing of the most intensive lines for α-Al_2O_3 and Cr_2O_3.

After firing at 650°C the open porosity and thermal strength were almost identical for all specimens regardless of the type of phosphate binder but the crushing strength was about 30% higher for specimens which contained the ACPB. After the repeat firing at 1600°C the properties of the specimens containing an ACPB, more especially that of composition No. 2, were better than those with the APB.

These results justified industrial scale trials with ACPB. Several batches of alumina — graphite nozzles with ACPB were produced at the NCP and tested successfully on CSC equipment at the NMP after which the NCP proceeded to use this binder for full-production purposes. The binder improves the molding properties of the batch so that the percent spoilage has fallen. Since these nozzles were introduced no miscasts due to faulty alumina-graphite nozzles have occurred on the CSC equipment. The erosion of nozzles with ACPB is less than for those with APB, i.e., by 0.03 mm/ton with killed steel and by 0.08 mm/ton for high-aluminum and tube steels.

The causes of the dissimilar behavior of APB and ACPB No. 1 were analyzed by heating the binders for 2 h at 650, 1100, 1300, and 1600°C in oxidizing and slightly reducing media in parallel. After each heat treatment the specimens were subjected to x-ray phase analysis and microscopy in an immersion liquid, and their P_2O_5 content was determined.

The diagram in Fig. 1 shows the heat-induced loss of P_2O_5 in APB and ACPB No. 1. The loss was more rapid for the latter, and in the slightly reducing medium the loss was greater for both binders.

The x-ray analysis showed that the phase composition of the binders varied considerably with the heat treatment temperature. The analysis was conducted on a DRON-1 x-ray diffractometer using the Cu K_α emission of a BS13-8 tube.

The phase composition of the specimens is given in Table 3 together with four to six interplanar spacings corresponding to the most intensive lines of the compounds concerned. According to Yvoire [10, 11], for aluminum metaphosphate $Al(PO_3)_3$ of modification A these lines are those with the interplanar spacings 4.35 (extremely strong), 3.67 (very strong), 3.43 (very strong), 2.93 (strong), and 2.69 (strong); for $Al(PO_3)_3$ of modification C those with the interplanar spacings 3.80 (extremely strong), 3.69 (strong), 3.60 (strong), 3.35 (extremely strong), 3.10 (strong), and 2.73 (strong); and for aluminum orthophosphate in cristobalite form the lines with the interplanar spacings 4.07 (extremely strong), 3.16 (medium strong), 2.87 (medium strong), and 2.51 (strong).

The phase composition of APB at 650°C is represented by aluminum metaphosphate in A form, the most stable one for $Al(PO_3)_3$. It dissociates with an increase in the temperature to give orthophosphate in cristobalite form most of which is converted to glass at 1600°C.

At 650°C, ACPB No. 1 consists of a vitreous product which is devitrified with an increase in the temperature to form metaphosphates and orthophosphates. The metaphosphate of this binder occurs predominantly in the C form which is more characteristic for chrome metaphosphates $Cr(PO_3)_3$. It appears that some of the aluminum is replaced by chrome so that the phosphates take the form of solid solutions of the type $(Al, Cr)(PO_3)_3$ and $(Al, Cr)PO_4$. The added chrome therefore stabilizes the metaphosphate in the C form and prevents the vitrification of the orthophosphate at high temperatures.

The dependence of the phase composition of the binders on the medium is not of a fundamental character and is attributable to the extensive dissociation of the phosphates in the slightly reducing medium (see Fig. 1). For example, at 1600°C in an oxidizing medium binder ACPB No. 1 consists of phosphate in cristobalite form but in a slightly reducing medium (remanent P_2O_5 content 0.8%) of the solid solution $Al_2O_3 - Cr_2O_3$.

An examination in an immersion liquid under the microscope confirmed the findings relative to the phase composition of the binders. The refraction indices of the aluminum metaphosphate are interesting. Metaphosphate of A modification consists of colorless isotropic grains of irregular shape with $N = 1.550$ approximately, and the solid solution of C modification of rounded grains with a slight birefringence $N = 1.654$. The refraction index of the glass of APB (1600°C) is 1.516 and that of the glass of ACPB No. 1 (650°C) 1.550. This marked difference in the refraction indices of the glass is evidence of differences in their nature and chemical composition.

The results of this investigation of the behavior of the binders on heating explain the differences in the properties and durability of nozzles with dissimilar phosphate binders.

The greater strength of the product with ACPB arises from the vitreous state of the binder during firing (650°C).

The larger proportion of vitreous phase in nozzles with APB (owing to the presence of clay in the phosphate binder) during casting compared with that in nozzles with ACPB evidently helps the steel to erode the binder and prevents the elimination of gases the pressure of which has a destructive effect on the nozzle. These factors degrade the service properties of nozzles with this binder.

The durability of the nozzles thus depends not only on the degree of dissociation of the phosphate binder but also on the state of the bond during firing and in the steelcasting operation.

Aqueous solutions of ACPB are more stable in storage than APB solutions, a contributing factor to a stable nozzle production process and less spoilage.

CONCLUSIONS

Nozzles for steelcasting are more durable when produced with an aluminochromophosphate binder than with an aluminophosphate binder, the reasons being the more favorable conditions for the preparation of the batch and the state of the bond during firing and in the steelcasting process. Nozzles containing ACPB No. 2 binder should also be produced and tested on an industrial scale.

LITERATURE CITED

1. A. N. Sokolov, L. G. Stochek, N. D. Karpov, et al., Authors' Certificate No. 342846. Byull. Izobr., No. 20, 69 (1972).
2. M. P. Dovnar, L. G. Stochek, B. G. Markelov, et al., Ogneupory, No. 8, 8-9 (1972).
3. S. L. Golynko-Vol'fson, M. M. Sychev, L. G. Sudakas, et al., in: Chemical Principles of the Technology and Use of Phosphate Binders and Coatings [in Russian], Khimiya, Leningrad (1968).
4. É. V. Degtyareva, Trans. Ukr. Scientific-Research Institute for Refractories [in Russian], No. 5, Metallurgizdat, Khar'kov (1961), pp. 290-298.
5. L. B. Khoroshavin, G. V. Dolgikh, and V. M. Ust'yantsev, Ogneupory, No. 8, 43-44 (1970).
6. G. A. Semenov, K. E. Frantseva, E. N. Nikolaev, et al., Ogneupory, No. 6, 52-55 (1974).
7. A. V. Bromberg, A. G. Kasatkina, V. A. Kopeikin, et al., Neorgan. Mat., 5, No. 4, 805-807 (1969).
8. W. D. Kingery, J. Amer. Ceram. Soc., 1, No. 8, 247-250 (1950).
9. T. Chvatal, Bol. Soc. Esp. Ceram., 7, No. 2, 165-167 (1968).
10. F. D. Yvoire, Bull. Soc. Chim. France, No. 10, 1762-1777 (1961).
11. F. D. Yvoire, Bull. Soc. Chim. France, No. 6, 1237-1243 (1962).