ALUMINA-GRAPHITE FUNCTIONAL REFRACTORIES IN STEEL CASTING APPLICATIONS BASED ON RESIN FREE BINDER SYSTEM

Patrick Gehre[1], Susann Ludwig[1], Christos G. Aneziris[1], Markus Braun[2], Winfried Boenigk[2], Christoph Jacob[2]
[1]TU Bergakademie Freiberg, Institute of Ceramic, Glass and Construction Materials, Freiberg, Germany, [2]RÜTGERS Germany GmbH, Castrop-Rauxel, Germany

ABSTRACT

The continuous casting sector of steel production is a common application field of Al_2O_3-C refractories, where they are used as functional components. Since several decades phenolic resin binder based systems are widely applied. In terms of this contribution a resin-free new hybrid binder system will be demonstrated which fulfills the extreme mechanical, thermal and chemical requirements of the application as stopper or submerged entry nozzle. Mechanical properties were evaluated at ambient and at elevated temperatures. In a first step a steel casting simulator was used to verify the interactions with a steel melt. Graphs based on computer tomography showed no cracks in spite the high thermal shock attack from room temperature to 1600 °C temperature of the steel melt. Based on the positive results demonstrators with dimensions close to real components were evaluated in an aggressive steel/slag-system in a foundry. The demonstrators survived several thermal shocks and no contamination of the steel was registered. The constitution after the foundry test opens the horizon for the new binder system to be used in advanced applications such as the continuous steel casting.

Keywords: alumina-graphite; carbonaceous resin; monobloc stopper; thermal shock

INTRODUCTION

In the steel casting industry, functional components based on alumina-graphite are suitable because they fulfill the demands during casting. They have to provide an excellent performance against thermal shock attack, aggressive molten slags, and molten metal. However, a major drawback is seen in the poor oxidation resistance leading to premature failure of the functional component. Alumina-graphite components contain antioxidants like fine metal/metal carbide powders (Si, Al, SiC, B_4C) to prevent carbon burn-out, and/or they are glazed externally [1][2]. Furthermore, the addition of metallic powders reduces open porosity and improves mechanical properties [3][4]. These improved properties are also beneficial to withstand corrosion and erosion by molten metal and slags. In detail, the decrease in open porosity can prevent infiltration of the component by molten slag and metal [5][6]. Tailored porosity can help to meet the request for improved thermomechanical properties. Another focus of the refractory industry is to fulfill ecological aspects without any drawback on chemical and thermomechanical performance of the functional components. This work illustrates the development of a new phenolic resin free binder system based on a combination of a modified coal tar pitch (carbonaceous resin) and a monosaccharide. The physical and mechanical property profile as well as the transfer of the self-glazing behavior like it is known for resin bonded material was of great interest. Investigations revealed that the new developed materials show comparable properties like those bonded with phenolic resin. Corrosion and erosion resistance were tested by applying dynamic finger tests. Due to the excellent corrosion and erosion resistance, monobloc stoppers based on the developed materials are highly recommended to be tested under industrial conditions.

EXPERIMENTAL

The raw materials used for sample preparation were fused alumina (0 - 0.2 mm, 99.70 mass% Al_2O_3, 0.16 mass% Na_2O), tabular alumina (0.2 - 0.6 mm, 99.50 mass% Al_2O_3, max. 0.40 mass% Na_2O) and two different graphites, a fine graded one with 99.5 mass% passing through 40 µm mashed sieve (96 – 97 mass% C) and a normal flake graphite with 95.0 mass% having a diameter greater than 71 µm (94 – 96 mass% C). A binder-combination of carbonaceous resin powder (30 mass%) and an aqueous fructose syrup (70 mass%) was used. A novolak type binder was used as reference. Hexamethylenetetramine (hexa) in a dosage of 5 mass% (10 mass% for phenolic resin) of the binder mass was added as curing agent. Additionally, two batches (fructose syrup and carbonaceous resin binder combination with and without TiO_2) were prepared without hexa. Additives like fine Si metal (0 – 75 µm, >97 mass% Si), SiO_2 (0.1 – 0.3 µm, >96 mass% SiO_2) and anhydrous borax (0 – 150 µm, >98 mass% $Na_2B_4O_7$) were the main additives for the self-glaze formation. TiO_2 (>99.5 mass%) was added to influence the oxidation resistance and the mechanical properties. Tab. 1 gives an overview of selected compositions considering different binder systems and use of additives.

Similar to commercial standard processing, monobloc stoppers were produced as follows: a) mixing all raw materials, b) forming by cold isostatic pressing with a maximal pressure of 100 MPa and finally c) carbonization under reducing atmosphere at 1400 °C and a dwell time of five hours using a retort filled with coke breeze. Before carbonization, the reference sample with phenolic resin as binder was cured at 180 °C. For corrosion tests, the samples covered by a formed self-glaze were used. To achieve a self-glazing effect, it was necessary to oxidize the samples at 1300 °C for 5 hours with a heating rate of 21 K/min.

Bars with shape 25 mm x 25 mm x 150 mm were cut to investigate the carbonized samples. Open porosity and pore size distribution were analyzed by using mercury intrusion porosimetry as well as by Archimedes principle using toluene as intrusion medium. Furthermore, mechanical properties like cold modulus of rupture (CMOR) were determined according to DIN EN 993-6. The corrosion resistance against molten steel was tested via dynamic finger test with bars of various compositions. Before corrosion test, the samples had to be glazed to get protected against carbon burn-out. Straight before immersion, the samples were pre-heated above the steel melt for 2 minutes. During the finger test a continuous argon flow inhibit oxidation. The glazed and pre-heated samples were immersed for 15 min and rotated slowly (30 rpm) within the molten steel. The temperature of the steel bath was kept constant at 1600 °C.

Due to the good results, monobloc stoppers were tested under industrial conditions in a steel foundry. The stoppers were immersed twice in molten steel covered with an acidic slag for about two minutes (5 min cooling between immersions). The temperature of the steel bath was in the range of 1700 °C.

RESULTS AND DISCUSSION

Tab. 2 summarizes physical and mechanical properties considering the different binder systems. The open porosity values were obtained with the aid of toluene penetration method (Archimedes principle). The reference sample has an open porosity of 18.4 %. Using fructose syrup and carbonaceous resin powder without hexa is a great advantage over using novolak resin. However, the open porosity values in Tab. 2 indicate that this will result in slightly higher open porosity. This disadvantage can be compensate by adding TiO_2. Materials without using TiO_2 have slightly higher OP values in the range of 19.4 to 21.1 %.

Tab.1: Compositions for producing monobloc stoppers (Fru - fructose; wH - without hexa; In - invert sugar).

	Fru-0.1	6C-Fru	TiO_2-Fru	Fru-0.1-wH	TiO_2-Fru-wH	In-0.1	TiO_2-In	Reference (resin)
	wt%							
Fused alumina	26.71	26.30	26.58	26.71	26.58	26.67	26.51	27.18
Tabular alumina	35.61	34.98	35.44	35.61	35.44	35.57	35.35	36.24
Graphite	17.80	15.97	17.72	17.80	17.72	17.78	17.68	18.12
SiO_2	3.56	3.75	3.54	3.56	3.54	3.56	3.53	3.62
Si (met.)	3.56	3.75	3.54	3.56	3.54	3.56	3.53	3.62
$Na_2B_4O_7$	1.78	2.01	1.77	1.78	1.77	1.78	1.77	1.81
TiO_2	-	-	0.62	-	0.62	-	0.64	-
Fructose	7.42	8.04	7.24	7.42	7.24	-	-	-
Invert sugar	-	-	-	-	-	7.53	7.48	-
Carbonaceous resin	3.56	5.21	3.54	3.56	3.54	3.56	3.53	-
Novolak resin	-	-	-	-	-	-	-	9.39
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Hexa	0.5	1.0	0.5	-	-	0.5	0.5	1.0
Additive	0.1	-	-	0.1	-	0.1	-	-

Tab. 2: Physical and mechanical properties of different compositions with the new hybrid binder system compared to resin bonding.

Composition	BD (g/cm^3)	OP (%)	CMOR (MPa)
Fru-0.1	2.45 ± 0.01	20.5 ± 0.1	9.0 ± 1.0
6C-Fru	2.4 3± 0.00	20.6 ± 0.1	10.2 ± 0.7
TiO_2-Fru	2.51 ± 0.01	18.3 ± 0.1	10.2 ± 1.5
Fru-0.1-wH	2.45 ± 0.02	21.1 ± 0.3	5.1 ± 1.7
TiO_2-Fru-wH	2.51 ± 0.01	18.5 ± 0.2	9.2 ± 2.0
In-0.1	2.46 ± 0.01	19.4 ± 0.3	8.7 ± 1.2
TiO_2-In	2.47 ± 0.01	18.9 ± 0.2	11.6 ± 1.2
Reference (resin)	2.50 ± 0.00	18.4 ± 0.1	8.4 ± 1.4

By comparing the cold modulus of rupture it is obvious that the new developed materials (with exception of sample Fru-0.1-wH) had slightly higher CMOR compared to the common resin bonded samples of these test series. TiO_2 containing samples show the highest CMOR, which indicates a strengthening due to phase formation (TiC, TiCN), as described in other reports [7].In Fig. 1 the pore size distribution of the new developed materials compared to a novolak resin bonded sample is shown. It is obvious that all new materials have a pore size distribution which is shifted to higher pore sizes.

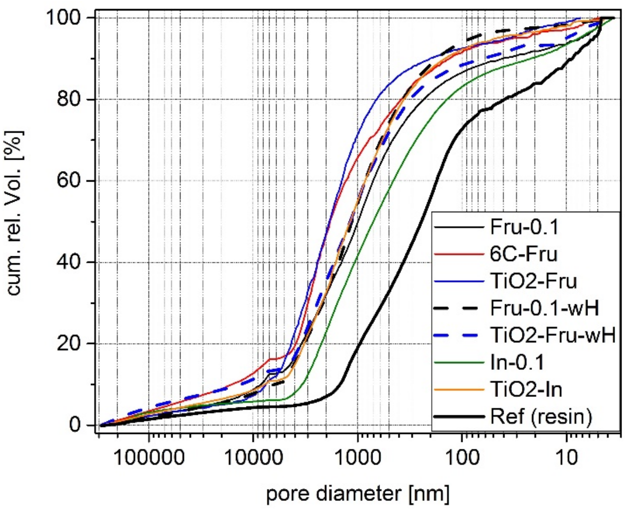

Fig. 1: Pore size distribution of samples with different binder systems after carbonization.

The median pore size (d_{50}) of the novolak resin bonded reference sample was the lowest one (248 nm). Samples Fru-0.1 and In-0.1 with d_{50} of 980 nm and 722 nm respectively are the only samples having d_{50} values smaller than 1000 nm. All other compositions had much higher d_{50} values up to 1850 nm (sample TiO_2-Fru).

In spite of the shift of the porosity to higher pore sizes in comparison to the phenol based resin bonded sample as a function of the additives, the open porosity remains at similar levels. Hence, due to the bigger pores a better thermal shock performance can be achieved. This is related to the fact that in case of refractories a slow growth of large voids as a function of the thermal shock is desired for an excellent thermal shock performance.

The functionality of the self-glazing behavior of the new-developed materials was of great interest. After firing in oxidizing atmosphere the mass loss of the bars reflects the quality of the self-glazing. Tab. 3 summarizes the mass loss after firing as a function of the composition. The new developed materials show comparable mass loss and self-glazing behavior like the reference sample with common novolak resin bonding. Especially samples Fru-0.1 and Fru-0.1-wH (without hexa) show a very similar mass loss. The slightly higher mass loss of samples 6C-Fru and In-0.1 can be explained by the higher open porosity compared to Fru-0.1 and Fru-0.1-wH. In contrast, all TiO_2-containing samples exhibit a higher mass loss even if the open porosity is low.

Tab. 3: Mass loss after firing in oxidizing atmosphere of different compositions with the new hybrid binder system or resin.

Composition	Mass loss (mass%)
Fru-0.1	1.86
6C-Fru	2.44
TiO_2-Fru	3.39
Fru-0.1-wH	1.66
TiO_2-Fru-wH	2.58
In-0.1	2.92
TiO_2-In	4.20
Reference (resin)	1.76

In a next step, it was of great interest whether the new developed materials are able to resist attacks by molten steel in combination with thermal shock. Fig. 2 shows a micrograph of a bar after the dynamic finger test. No crack formation but a crystal growth on the self-glaze could be observed by digital microscopy.

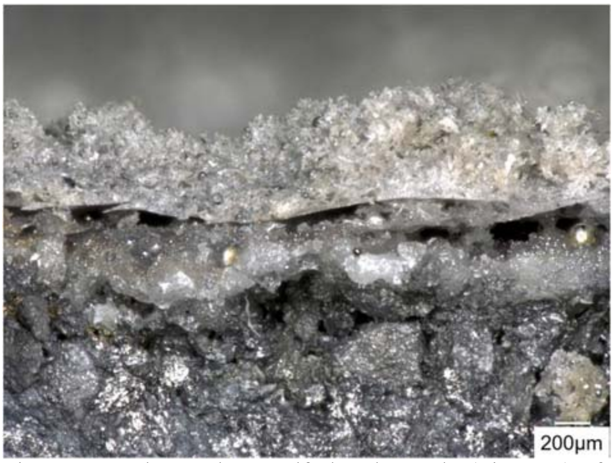

Fig. 2: Crystal growth on self-glazed sample (TiO_2-Fru) after dynamic finger test (100x magnification).

Fig. 3 shows a SEM cross section of sample 6C-Fru after the immersion test. The formation of a new crystal phase on top of the refractory surface can be seen. Additionally, steel droplets adhere on the refractory surface, but no wetting or intrusion could be observed.

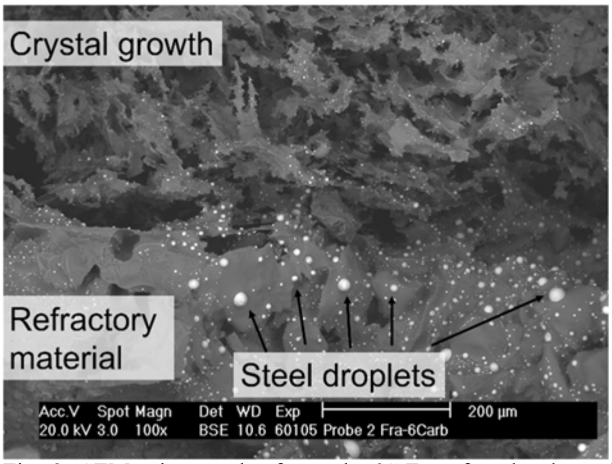

Fig. 3: SEM micrograph of sample 6C-Fru after the dynamic finger test.

For the phase identification of the new phase formation, energy dispersive X-ray diffraction (EDX) was performed. Fig. 4 displays a SEM micrograph of sample Fru-0.1 with related EDX analysis. According to EDX analysis, the new phase consists of secondary formed Al_2O_3. The phase formation is likely a result of a clogging-like process and contains a secondary in situ formed Al_2O_3. A model for this mechanism is described in [8].

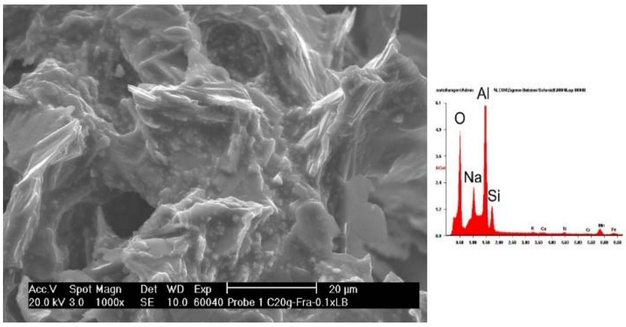

Fig. 4: SEM micrograph (left) and EDX analysis (right) of sample Fru-0.1

Following successful finger tests, the monobloc stoppers were tested under industrial conditions. After two steel/slag applications, the stoppers were cut lengthwise to evaluate any erosion or corrosion (Fig. 5). Only slight erosion by molten steel and/or slag takes place. This slight erosion may also result from mechanical slag remove. An important aspect is the excellent thermal shock resistance. During each immersion for 2 minutes, the stopper cooled for 5 minutes. It is remarkably that the monobloc stopper withstood a temperature difference of about 1700 K without any crack formation.

Fig. 5: Monobloc stopper (TiO_2-Fru) after immersion test under industrial conditions.

Tab. 4 gives an overview of the steel bath composition before and after the immersion test. No significant changes of the composition due to corrosion effects were observed.

Tab. 4: Chemical composition of the steel before and after immersion test.

	Chemical composition (wt.-%)	
	Before immersion	After immersion
C	0.203	0.210
Si	0.377	0.373
Mn	0.768	0.736
P	0.011	0.012
S	0.009	0.008
Cr	0.136	0.149
Ni	0.080	0.081
Mo	0.028	0.028
Al	0.004	0.002
Co	0.008	0.008
V	0.007	0.007

CONCLUSION

In this work a new developed phenolic resin-free binder system composed of carbonaceous resin powder and aqueous fructose syrup was introduced. Physical and mechanical properties of developed compositions with varying binder and TiO_2 portion as well as with and without hexa were evaluated. In comparison with phenolic resin bonded materials similar open porosity can be achieved if fructose syrup and carbonaceous resin powder without hexa in combination with TiO_2 is used. Furthermore, the new developed materials provide slightly higher CMOR compared to the common resin bonded samples. Hence, hexa addition and annealing is not necessary anymore. In a further step corrosion and erosion performance was studied with the aid of a dynamic finger test in full controlled atmosphere. The new developed material presents a very good thermal shock behavior and only slight corrosion or erosion. Due to the excellent behavior during the dynamic finger tests, testing under industrial conditions in a foundry was performed. The applied monobloc stopper showed comparable corrosion/erosion behavior and only slight material degradation. In addition, all immersed stoppers withstood thermal shock of about 1700 K.

By applying a binder system composed of carbonaceous resin powder and aqueous fructose syrup, the microstructure shows larger voids indicated by a shift of the porosity to higher pore sizes in comparison to phenol based resin bonded reference sample. However, this larger pore sizes have no negative effect on the strength and open porosity as CMOR as well as open porosity values of samples with TiO_2 addition, even without the use of hexa, are in range of phenol based resin bonded reference sample. Greater pore sizes in a refractory material in combination with CMOR and open porosity staying in the same level even has a great advantage: a slower crack growth of larger voids present in the microstructure will increase the thermal shock resistance. This effect was proven in the foundry tests.

The new phenol resin free binder system based on the additive combination, and which is free of hexa, opens the horizon for excellent thermomechanical and chemical properties at elevated temperatures. It is ideal for short- as well as long-term application times due to its high amount of graphitic like structures.

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