Influence of carbores binder on the strength of Magnesia-Carbon materials

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Keywords: carbores binder,magnesia-carbon,strength, environment-friendly.

Abstract. A new binder system was developed to produce Magnesia-Carbon matreials in a cold batch process. The binder system comprises a liquid carbores and a high-melting carbores powder. Both components are graphitizable thus leading to an anisotropic carbon system resistant to spalling and oxidation. The system combines the processing advantages of a resin-based binder and the high performance of a pitch based binder. The binder system complies with the stringent requirements of TRGS 551(the level of benzo[a]pyrene well below 50 mg/kg). Lab tests indicated the viscosity of the liquid carbores allows a mixing process at room temperature, the medium and low temperature strength level of the new bonding system is comparable to pitch-bonded bricks and allow safe handling and lining.

Introduction

For the production of magnesia-carbon materials either coal tar pitch or phenolic resin is used as a binder. The superior performance of pitch-bonded bricks is related to the anisotropic, graphitizable coke structure of pitch after carbonization[1]. This mechanieal flexibility of the coke structure results in higher spalling resistance, better thermoshock stability and a higher strength at working temperatures. Pitch-bonded bricks are widely produced in Europe while they are not very common in Asia. The production of pitch-bonded bricks requires a hot mixing process and the standard coal tar pitch is considered hazardous for the environment due to the presence of toxic polyaromatic hydrocarbons like benzo[a]pyrene (B[a]P). The content of B[a]P in coal tar pitch ranges from 10,000 to 15,000 mg/kg. A recently developed new type of carbonaceous resin (CARBORES@ F) has a B[a]P content of below 300 mg/kg and allows the production of pitch-bonded bricks with less than 10 mg/kg B[a]P thus meeting the EU regulation TRGS 551 [2, 3, 4]. However, CARBORES@ F still requires a hot mixing process.

In former work the soft bonding system have been studying by a combination of liquid phenolic resin and the carbores powder. the binder coke to some extent becomes anisotropic after carbonization resulting in an improved mechanieal flexibility and better oxidation resistance[5,6,7]. In most cases the replacement of phenolic resin powder by the carbores powder will reduce the cost for the total bonding system.An additional cost saving is usually achieved due to the fact that the soft bonding allows to reduce the amount of anti-oxidants . The amount of carbores powder may vary between 0.5 and 2%.The complete or partial substitution of powder resin results in lower strength after curing. This is compensated or even over compensated during carbonization[8,910].

In this lab test，we adopt dual carbores bonding systems and Carbores/Resin bonding systems to

produce Magnesia-Carbon samples, compared the physical index：bulk density , CCS （pressing）, bulk density，porosity，CCS （hardening）, bulk density，porosity，CCS and PLC （coking）, study the strength change of different bonding systems at medium and low temperature.Lab tests indicated the viscosity of the liquid carbores allows a mixing process at room temperature, and the strength level of medium and low temperature for the new bonding systems is higher than that of resin-bonded samples and allow safe handling and lining.

Experimental

The bonding system are compared in accordance with the scheme described in Table 1.

Tab. 1. Batches

batches	1and 2	3 and 4	5 and 6
Liquid resin		○	
Resin Powder			○
Garbores Powder	○	○	○
Liquid Garbores	○	○	○

Raw materials

For all tests magnesia-carbon model batch is used. The granulometric composition of the mixture was chosen for an optimal packing tightness with a max. Particle size of 5-0 mm. Each batch consists of highpurity fused magnesia, flake graphite and binders. The raw materials have properties according to Table2.3.4.

Tab.2. Properties of the dry raw materials used

material	B.D g/cm^3	MgO %	SiO_2 %	CaO %	Fe_2O_3 %	B_2O_3 %
Fused Magnesia	3.5	97.6	0.85	0.88	0.62	0.01

Tab. 3. Properties of resol and Novolak

binder	resol	Novolak
Viskosity at 20°C [mPas]	1500±150	
Non-volatile matter at 135°C [%]	80±5	
Water content Karl-Fischer [%]	≤3	
Free phenol [%]	≤5	≤5
Flow distance [mm]		16±4
Hexa content [%]		10±1
Particle size > 0.045 mm [%]		11±3
Bulk density [g/dm^3]		365

Tab. 4. Properties of carbores

binder	CarboresP	CarboresT
Description	**Powder**	**Liquid**
Glass transition temperature [°C]	213	
Coking value (ISO 6998) [%]	85.5	32
Benzo[a]pyrene content [mg/kg]	300	300
Granulometry(＜200 u m) [%]	90	
Dynamic viscosity at 20°C[mPas]		3200

Production of batches and sample preparation

The bonding systems according to Table 1 are evaluated. The targeted carbon content of the carbonized brick is 12-13%. All components are added and mixed in the sequence given in Table 5. The total mixing time is 15 minutes. After a maturation of 2 hours in a closed vessel the batches are pressed to cylindrical （Φ50×50mm）and strip specimen （25×25×125mm） in a hydraulic press at 200MPa. Specimens are tempered in normal atmosphere up to 180℃ according to a temperature profile typically used for resin-bonded bricks. After tempering all specimens were carbonized in inert atmosphere by heating up to 400℃,600℃,800℃ and 1000℃ respectively and a final holding time of 5 hours.

By using three-point bending machine, Hot modulus of rupture (HMOR) can be tested，testing furnace was heated up to 400℃,600℃,800℃, 1000℃ and 1400℃ in inert atomphere and the final holding time is 30min, the speed of increase the load at 10N.min-1, until the point of rupture.

Tab. 5. Composition of batches and mixing sequence

sequence	batch	component	Amount[%]	Total[%]
1	all	Fused magnesia 3-5mm	25	25
2	all	Fused magnesia 3-1 mm	20	45
5	all	Fused magnesia 1-0 mm	20	65
7	all	Fused magnesia 0.088mm	25	90
4	all	Flake graphit	10	100
3 6	1	CarboresT CarboresP	+2.0 +1.3	103.3
3 6	2	CarboresT CarboresP	+2.5 +1.5	104
3 6	3	Resol + CarboresT CarboresP	+1.5+1.5 +1.3	104.3
3 6	4	Resol + CarboresT CarboresP	+1.5+1.5 +1.5	104.5
3 6	5	CarboresT CarboresP + Novolak	+2.0 +0.7+0.7	103.4
3 6	6	CarboresT CarboresP + Novolak	+2.5 +0.8+0.8	104.1

Results and discussion

Density, cold crushing strength and porosity

Results on bulk density, porosity, permanent linear change and cold crushing strength measured at room temperature are shown in Table 6. The Resin/Carbores sample show the highest densities. The Carbores/Resin powder sample are slightly lower while the the dual carbores sample show the lowest . Apparently, this does not translate into inferior product properties.

After tempering the resin/carbores sample have the highest strength while for carbores the strength is lower. This can be explained by the fact that both the liquid carbores as well as the

carbores powder do not cure at tempering temperature. After carbonization, the strength level is comparable to pitch-bonded bricks.

Tab. 6. Results on specimens after moulding, hardening and coking

batch		1	2	3	4	5	6
After pressing	CCS[KN]	21	20	27	29	18	16
	B.D[g/cm^3]	2.92	2.99	2.99	2.98	2.94	2.94
After hardening/ tempering	CCS[MPa]	61	68	72	75	72	66
	B.D[g/cm^3]	2.95	2.94	2.94	2.95	2.91	2.91
	OP[%]	7.6	6.9	5.9	5.2	8.1	7.5
After coking	CCS[MPa]	41	41	54	43	37	40
	B.D[g/cm^3]	2.86	2.87	2.85	2.85	2.89	2.83
	OP[%]	13.3	12.0	12.4	13.0	12.1	12.7
	PLC in PD [%]	0.15	0.21	0.18	0.33	0.1	0.17
	PLC⊥PD [%]	0.09	0.05	0.15	0.16	0.01	0.01

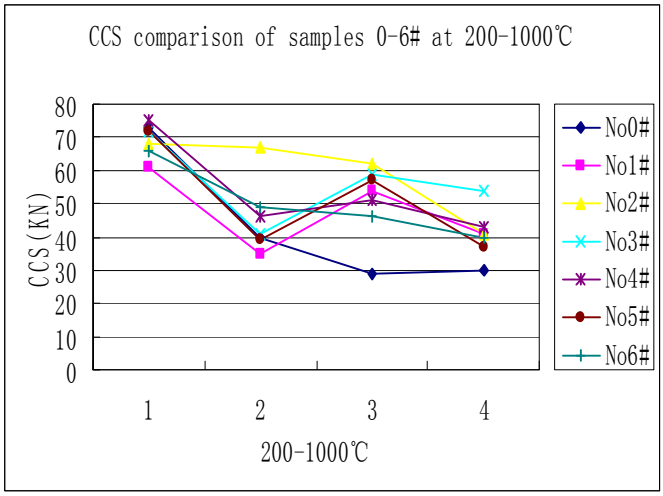
CCS = Cold Crushing Strength, BD = Bulk Density, OP = Open Porosity, PLC = Permanent Linear Change, in PD = in press direction,
⊥PD = perpendicular to press direction

It indicates that all samples keep good moulding function.Compared to pure resin binder sample with 3.5% liquid resin， Quantity of 1.5-2.0% Carbores liquid binder can meet the moulding requirement well.

Strength variation at different temperature

Fig1 shows the development of the CCS versus temperature of specimen .As fig 1 shows, No 2# shows difference strength variation(temperature range of 400-600℃) Compared to the other binder methods，It gets the highest strength value among all the bonding methods，which is the low point to traditional resin bonding.The strength value of No1#,3#,4#,5# rise apparently (temperature range from 400 to 600℃). In all test samples, batch 2# and 3# have good synthesized physical index (No 0# is pure resin binder samples).

fig 1 Strength Comparison at different tempering temperature



HMOR variation comparison

Fig 2 shows modulus of rupture (HMOR) comparison of different bonding samples at 200℃,400℃,600℃,1000℃.As result shows,the HMOR value of all test samples apparently higher than that of resin bonding No0#. The increase of strength at temperature range above 400°C results from the development of a semi-coke structure and later by the final coke structure.

fig 2 HMOR comparison at 200-1000℃

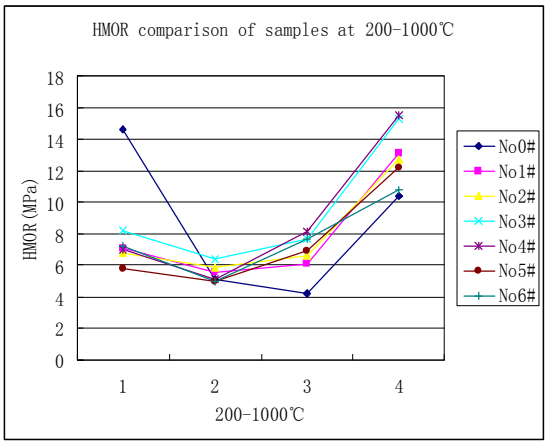


fig 3 HMOR comparison at 1400℃

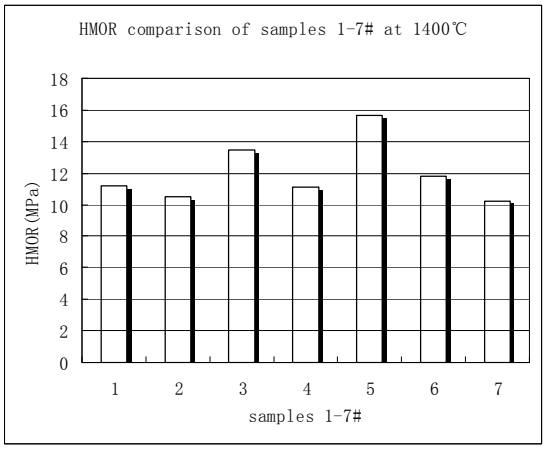


Fig 3 shows hot modulus of rupture (HMOR) comparison at 1400℃， As result shows, the HMOR value of all samples is comparable with sample 7#, expecially notice that the HMOR value of sample 7#(with antioxidants) is relatively lower.

The strength-temperature curve can be explained by the fact that the solubility of carbores powder in the liquid carbores raise with increasing temperature and leads to a better wetting of the matrix and therefore to an increase of the strength. On the other hand with rising temperature more and more volatile components evaporate and create new porosity. These contrary reactions lead to a lower strength in the range of 200-400℃. The increase of strength at temperatures range above 400°C results from the development of a semi-coke structure and later by the final coke structure.

Conclusions

In laboratory scale it was shown that the bonding system consisting of a liquid Carbores and a Carbores powder provides results comparable to the existing bonding systems. the viscosity of the liquid carbores allows a mixing process at room temperature, the medium and low temperature strength level for the new bonding system is comparable to pitch-bonded samples and allow safe handling and lining. the new carbores binder belong to environment-friendly materials. The number of tested recipes still leaves room for further optimization， Large scale industrial trials have started to confirm the laboratory results.

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