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ALUMAGCARBON BRICKS WITH DIFFERENT ALUMINA AGGREGATES – TECHNICAL PROPERTIES AND INDUSTRIAL APPLICATION RESULTS WITH A NEW SINTERED AGGREGATE

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ABSTRACT
This paper investigates the spinel formation and technical properties of AluMagCarbon (AMC) bricks based on fused and sintered alumina aggregates. Special focus was given to a new European based sintered aggregate with 96% Al_2O_3 (BSA 96). The microstructural changes due to the spinel formation are related to the macroscopic brick properties and differ between fused and sintered alumina aggregates. Industrial application results from two ArcelorMittal steel works in Poland are reported.

INTRODUCTION

AluMagCarbon (AMC) bricks have become a common material for steel ladle linings. They are used in demanding places such as the impact area in the bottom and side wall but they are also used for complete ladle lining in bottoms and sides walls, except for slag lines. Spinel formation during use is a key feature of AMC bricks. This is essential for their high wear resistance. It continuously creates a slight expansion at the hot face of the bricks, which helps in overcoming opening of joints in the brickwork due to thermal cycling of the steel ladles. In addition, the spinel formed has high refractoriness and slag resistance and therefore helps to protect the thin de-carburised layer from corrosive wear.

Experience shows that in the side wall and bottom, except impact areas, the expansion behaviour is more important for the performance of the AMC bricks than is resistance against corrosion. Unstable and excessive expansion leads to spalling and accelerated wear of the lining[1]. Typically, the permanent linear change (PLC) at 1600°C, fired for five or ten hours in reducing conditions, is adjusted to + 1-2%.

Different alumina aggregates can be used as a basis for AMC bricks. These range from bauxite and brown fused alumina (BFA) to synthetic alumina based aggregates such as tabular alumina (TAB) or white fused alumina (WFA). The chemical purity of the aggregate has a significant influence on the wear resistance. Therefore higher purity aggregates are used in the most demanding areas, e.g. the bottom impact area. BSA 96 (BSA), a sintered aggregate with 96-97% Al_2O_3 was introduced as a new alternative in 2011[2]. The influence of the alumina aggregate on the spinel formation during firing and on the final brick properties have been investigated in this paper. Bauxite based bricks were not included because of a general lower level of performance when compared to the other higher purity alumina aggregates.

ALUMAGCARBON (AMC) TEST BRICKS

The test brick formulations based upon the four different alumina aggregates WFA, TAB, BFA, and BSA are given in table 1. Magnesia content and matrix formulation were identical for the tests. The BFA brick shows higher amounts of silica and titania due to a higher impurity level of the fused aggregate when compared to BSA. Larger quantities of test bricks were produced in standard format 25/0 (250x150x100mm) on the regular production line. Each brick was measured by ultrasound after tempering in order to select bricks that were within a range of two sigma from the Gaussian median for further investigation.

Tab. 1: Composition of test bricks

	WFA	TAB	BFA	BSA
Components	[wt%]			
WFA	79.8			
T60/T64		79.8		
BFA			79.8	
BSA 96				79.8
Fused Magnesia	9	9	9	9
Graphite	3	3	3	3
Matrix (C-bond, aluminium,calc. alumina)	8.2	8.2	8.2	8.2
Chemistry	[wt%]			
Al_2O_3	89.6	89.6	86.7	88.3
MgO	9.67	9.72	9.09	9.54
SiO_2	0.24	0.22	1.41	0.8
Na_2O	trace	trace	trace	trace
Fe_2O_3	0.12	0.15	0.25	0.19
TiO_2	trace	trace	1.99	1.08
LoI 950°C	6.22	6.69	5.98	6.9

Properties of the test bricks are given in table 2. Cylindrical samples 50x50mm were fired in reducing conditions at different temperatures and tested at the Ceramics Research Center of TATA Steel, IJmuiden, NL. The hot modulus of rupture (HMoR) at 1450°C was measured at Arcelor Mittal Refractories after pre-firing for ten hours at 1500°C in reducing conditions. Properties at 1600°C are most relevant because they refer to conditions at the hot face of the steel ladle lining.

The BFA brick has the lowest apparent porosity (AP) after tempering and also after firing at 1600°C. The BSA brick shows higher AP when fired at higher temperatures. This is partly due to the AP of the BSA 96 aggregate itself (4.4%). However, these pores are very small, having a median pore diameter of 0.4 µm and two thirds of pores smaller than 1µm (mercury intrusion at DIFK, Germany). For comparison, tabular alumina T60/T64 has 1.5% AP and 0.7 µm median pore size. BFA and WFA have 28 µm and 47 µm median pore size respectively, so much larger pores than the sintered aggregates.

HMoR of the test bricks at 1450°C is on a comparable level. In this case, bauxite based bricks have a significantly lower HMoR of only about 2MPa. This is due to the higher impurity level.

PLC (figure 1) shows a distinct difference between the BFA and BSA bricks, BFA shows 2.1% at 1600°C but with BSA it is 2.7%. BSA also shows stronger increasing PLC above 1300°C when compared to the other aggregates. Mineralogical investigations of fired bricks were carried out in order to explain these differences.

Tab. 2: Properties of tempered and fired AMC bricks (reducing conditions)

fired AMC bricks			WFA	TAB	BFA	BSA
Temperature						
BD	230/5h	g/cm³	3.23	3.11	3.32	3.15
	1000/5h		3.18	3.08	3.24	3.1
	1100/5h		3.16	3.07	3.25	3.13
	1200/5h		3.16	3.08	3.25	3.08
	1300/5h		3.15	3.06	3.24	3.07
	1400/5h		3.1	3.02	3.21	2.98
	1500/5h		3.09	2.97	3.17	2.9
	1600/5h		3.04	2.94	3.08	2.85
AP	230/5h	%	6.2	5.3	3.2	4.6
	1000/5h		12.4	10.8	8.7	9.8
	1100/5h		11.5	9.8	8.3	10.1
	1200/5h		11.7	10.2	8.7	10.5
	1300/5h		13	11.5	9	11.4
	1400/5h		13.3	12.6	10.1	16
	1500/5h		14.1	14.5	11.2	18.6
	1600/5h		14.8	15.7	12.5	19.6
CCS	230/5h	MPa	63	77	70	85
	1000/5h		23	41	34	51
	1100/5h		25	45	29	49
	1200/5h		25	41	29	43
	1300/5h		25	43	33	44
	1400/5h		21	43	32	34
	1500/5h		26	41	31	25
	1600/5h		20	44	45	32
HMoR	1450 °C	MPa	6	7	5	5

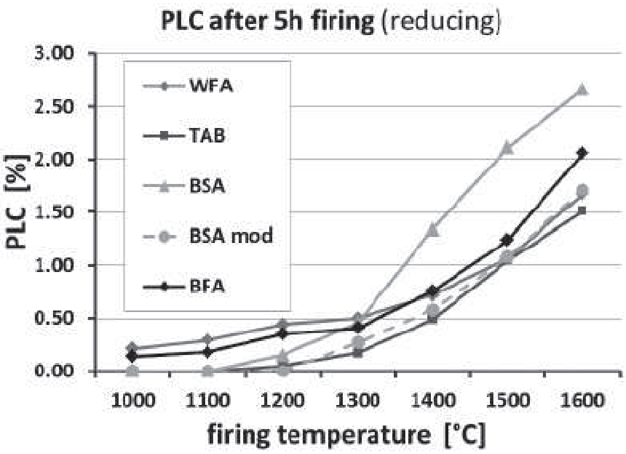

Fig. 1: Permanent linear change of AMC bricks, fired under reducing conditions for 5 hours.

SPINEL FORMATION IN AMC BRICKS

Spinel formation in the fired test brick samples was investigated at DIFK Germany, using X-Ray diffraction, reflected light microscopy, SEM and EDX. BSA shows a more intense spinel formation when compared to BFA and the other aggregates. This is shown in figure 2. The residual peak of periclase (MgO) at 1500°C is clearly lower for BSA than it is for BFA.

For the microstructure investigations, bricks containing both aggregates, BFA and BSA 96, and also WFA and TAB were investigated in order to compare their behaviour under identical conditions. BFA and BSA 96 (figure 3) show the typical microstructures of fused and sintered aggregates.

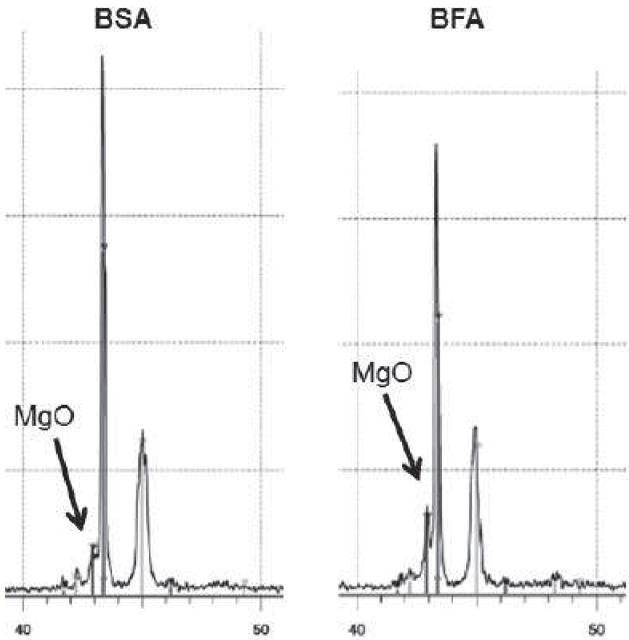

Fig. 2: XRD of AMC bricks BSA and BFA after 1500°C / 5 h reducing conditions; different periclase (MgO) peak height.

There are fewer, but larger pores in BFA and impurities tend to be concentrated in specific areas. Whereas with BSA 96 the pores are smaller and the impurities more evenly distributed. Also the majority of pores in BSA 96 are closed pores. At 1400°C, spinel formation is visible at the surface of the alumina aggregate grains. These are indicated by arrows in the picture. It is clear at 1400°C but also at 1500°C, that the spinel formation is more intensive and more homogeneous with BSA 96 than with BFA grains. At 1500°C, the spinel layer is about 80µm with BSA 96 but between 0 and 50 µm with BFA. At 1600°C, BSA 96 grains have a 100µm layer of spinel at the surface, and BFA between 0 and 100µm.

Figure 4 shows EDX analysis of the BFA/BSA brick fired at 1600°C. The different spinel layer formation is obvious here too. Spinel formation with BFA grains is more intensive in areas of enriched impurities, but it is hampered in purer areas. Two factors result in the more homogeneous spinel formation with BSA 96 than with BFA: the evenly distributed impurities and the small, homogeneously distributed pores in the structure of the sintered aggregate.

The spinel formation of WFA and TAB after firing for five hours at 1600°C is comparable as shown in figure 5. The spinel layer thickness is up to 50µm but is lower when compared to the less pure aggregates BFA and BSA 96. This proves the influence of traces of impurities on the spinel formation. The high amount of impurities in bauxite strongly contributes to a strong but unstable and less predictable spinel formation in bauxite based AMC bricks. On the contrary, AMC bricks with BSA 96 have stable and reproducible spinel formation, which also shows in stability of behaviour during production and use, and also when compared to BFA.

The microstructure pictures confirm the difference of spinel formation between AMC bricks and spinel forming castables, which has been reported by Schönwelski [3]. In AMC bricks, MgO becomes unstable at high temperatures and reducing conditions, and the formation of magnesium vapour leads to spinel formation at alumina aggregate grains even without direct contact with the magnesia grains. Spinel formation in carbon free castables requires such direct contact.

Additional investigations with a modified formulation of the BSA test brick have shown that it is possible reducing the PLC at 1600°C to e.g. +1.7% by reducing the magnesia content (see BSA

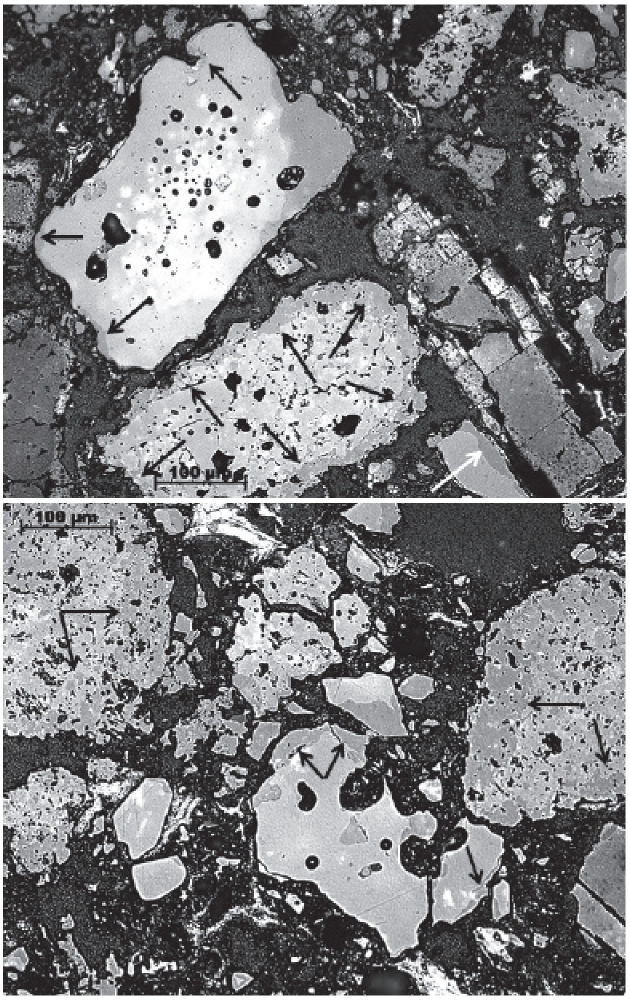

Fig. 3: Reflected light microscopy of BSA 96 and BFA grains in AMC brick fired 5 h in reducing condition at 1400 °C (up; periclase grains in lower left and right corner) and 1500 °C (down), see text.

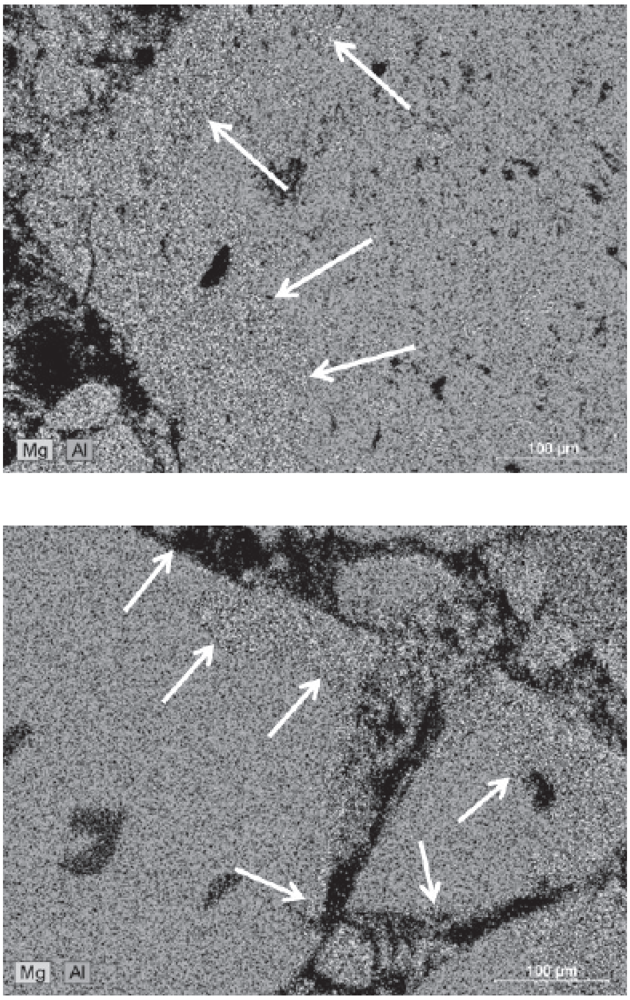

Fig. 4: EDX of BSA 96 (up) and BFA (down) grains in AMC brick fired at 1600 °C / 5 h in reducing conditions.

mod in figure 1). However, industrial results with the BSA brick proved no disadvantage of the higher PLC. So no industrial trials were made with the modified BSA brick yet.

Thermomechanical Testing

Figure 6 shows dilatation curves of the tempered bricks up to 1600°C including a holding time of six hours, and cooling thereafter (TATA Steel IJmuiden, NL). The effect of spinel formation and its kinetic on the expansion of the bricks is clearly visible. Spinel formation in TAB and WFA starts at about 1400°C but is quicker for TAB than for WFA.

For TAB it is completed when a temperature of 1600°C is reached, whereas WFA requires the holding time at 1600°C for quantitative formation of spinel. BSA also shows faster spinel formation when compared to BFA, and a slight compression during the holding time at 1600°C.

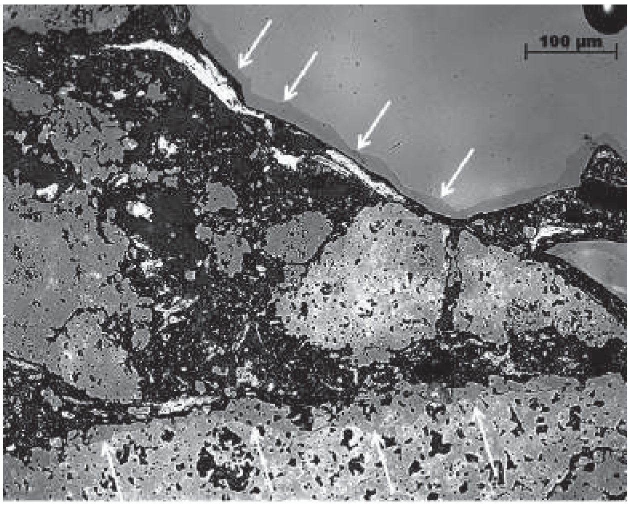

Fig. 5: Reflected light microscopy of TAB and WFA grains in AMC brick fired at 1600 °C / 5 h in reducing conditions.

TRIALS IN STEEL LADLE

BSA based AMC bricks from the study were used for steel ladle trials in two ArcelorMittal steel works: for bottom lining at ArcelorMittal Steel Kraków, except for the impact area, and for side wall lining in the metal zone at ArcelorMittal Steel Dąbrowa Górnicza.

In Kraków, the capacity of the ladle is 145 tonnes of steel. The average tapping temperature is 1668°C, and average holding time per heat is 129 minutes. The steel is aluminium killed in secondary metallurgy, and CaO/Al_2O_3 ratio of the slag is around 1.1.

Initially, a bottom was lined, half with BSA and half with BFA bricks. No differences were seen in performance. Thereafter, three complete bottoms (except impact area) were lined with BSA bricks. All bottoms worked without any problem up to the end of the campaign (130-140 heats). In all cases ladles were stopped due to wear of slag zone and/or impact area. A negative impact of the relatively high PLC of BSA bricks could not be seen.

The ladle in Dabrowa Górnicza is much bigger having a capacity of 320 tonnes of steel, and the conditions for the refractory lining

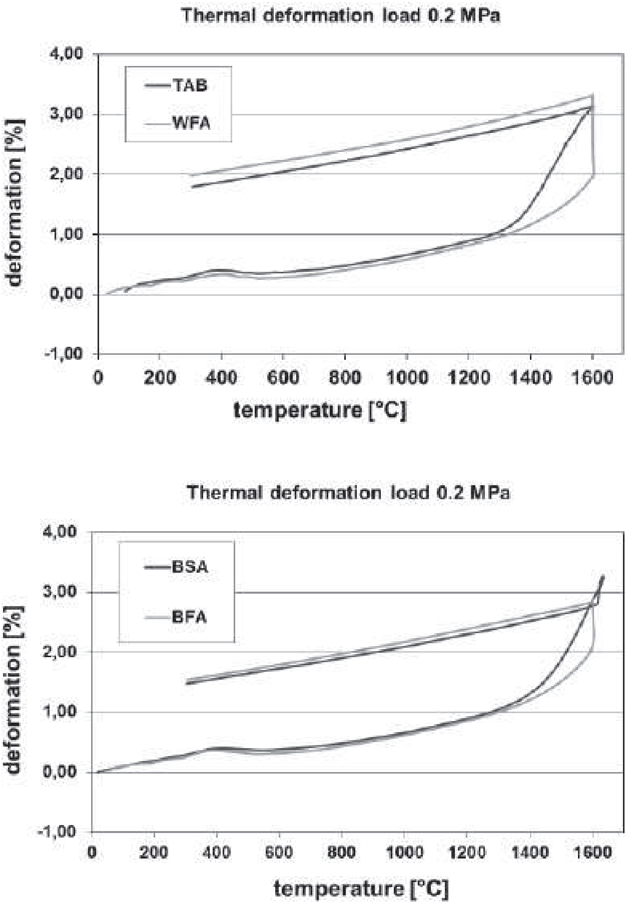

Fig. 6: Dilatation of AMC bricks in reducing condition, load 0.2 MPa, 6 h holding time at 1600°C; TAB and WFA (up); BSA and BFA (down).

are overall harder than in Kraków. The average tapping temperature is 1685°C and average holding time is 215 minutes. Commonly, steel is reheated in ladle furnace. The steel is mainly aluminium and sometimes silicon killed. The ratio of $CaO/Al_2O_3+SiO_2$ is around 1.2

The lining life and wear rate of BSA bricked ladles (table 3) were in the same range as the standard BFA bricked ladles. In all cases the wear in other areas of the ladle determined the lining life.

Tab. 3: Results from trials in ladle side wall of Dąbrowa Górnicza steel works.

Test period	Number of ladles tested	Average life time [heats]	Avg. wear rate [mm/heat]	Reason for stop
4Q/2015	3	73	1,0	slag line
1Q/2016	4	75	0,9	slag line

BSA bricks from the trial were investigated after use by X-ray diffraction (figure 7). The spinel formation is more pronounced with increasing temperature towards the hot side of the sample. Periclase (MgO) is consumed during this process. The shift in spinel peak indicates enrichment in Al_2O_3 content of the spinel.

THERMAL CONDUCTIVITY AND HEAT LOSSES

During treatment and transport of steel in the ladle, it cools by typically around 1K/min. For the heat losses influenced by the refractory lining two major mechanisms must be considered as described by Ogata et al.[4]. One is the heat transport through the lining to the steel shell, where it gets lost by radiation. The other one is the heat stored in the hot side of the wear lining, which partly gets lost by radiation during the empty times of the ladle cycle. The heat loss through the steel shell is primarily dependent from the setup of the permanent lining including an insulation layer. The heat loss due to thermal cycling at the hot face inside the ladle depends from the specific heat capacity of the wear lining material, so primarily its density, and the thermal conductivity of the wear lining material. The higher the density and the thermal conductivity, the more heat can get lost during the empty phases of the ladle. Accordingly, more heat from the liquid steel will be needed for reheating this layer in the next filled ladle stage and thereby increasing the temperature loss of steel.

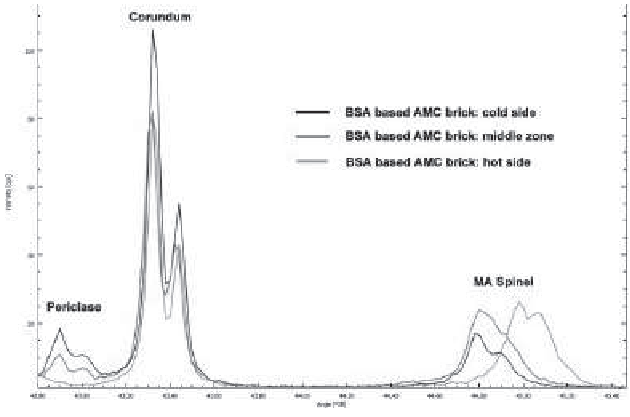

Fig. 7: Temperature dependent formation of Spinel in BSA based AMC brick from the ladle side wall trial.

After firing, the bulk density of BSA bricks is about 8% lower vs. BFA bricks, so the specific heat capacity is lower accordingly. Thermal conductivity measurements with the hot wire method show that the AMC brick with BSA 96 has lower thermal conductivity when compared to the AMC brick with BFA, e.g. 4.8 vs. 6.8 W/mK at 1200°C. The bricks were fired in reducing conditions at 1500°C prior to the measurement.

Thermal modelling comparing the BSA and the BFA bricks in the ladle side wall was carried out at TATA Steel Ceramics Research Center in IJmuiden, Netherlands. The transient FEM analysis of a generic steel ladle in that model is briefly described in [5]. Model results show, that the final steel temperature with BSA bricks is 2K higher when compared with BFA bricks. This may appear a small difference only, however, 2K additional steel temperature loss account for 10-20 Euro ct higher cost per tonne of steel as discussed by Buhr et al.[6].

CONCLUSION AND OUTLOOK

For the spinel formation in AMC bricks impurities and microstructure of the alumina aggregate are important. Traces of impurities support the spinel formation, which takes place not only in direct contact of alumina and magnesia but also through magnesium vapour diffusion. Sintered aggregates show a more even spinel formation when compared to fused aggregates due to their higher sintering activity. BSA 96 contains less but more evenly distributed impurities than BFA. Therefore BSA 96 shows predictable and consistent behaviour in spinel formation and PLC of AMC bricks. Expansion behaviour and thermo-mechanical properties can be changed by adjustment of magnesia content of the bricks. Based on positive experiences with AMC bricks containing blends of fused alumina aggregates with BSA 96, a pure BSA 96 brick was developed and successfully tested in practice in two steel works, both in the bottom and in the side wall. In both cases, the BSA based bricks achieved comparable wear rates as the standard BFA based bricks, and in all test ladles other lining areas such

as the slag line or the impact area were the reason for ending the ladle campaign. BSA based bricks are now qualified accordingly. Predictable expansion behaviour (PLC) of AMC bricks during use is essential for good performance in the steel ladle and is a prime focus in development and quality control. BSA 96 provides stable raw material properties, which enable smoother and controlled production and predictable and reliable performance.
The lower bulk density and thermal conductivity of AMC brick with BSA 96 when compared to BFA could reduce heat losses in steel ladles as shown by model calculations. This parameter is gaining increasing importance for steel companies who are looking to reduce energy consumption and CO_2 emission in steel production.

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