EFFECTIVENESS OF FIRED ALUMINA-SPINEL BRICK IN SECONDARY METALLURGY

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ABSTRACT

Alumina-Spinel fired refractory brick for steel ladle metal zone lining is one of the recent innovations over the last decade. The purpose of such innovation was primarily to cater the growing need of advanced metallurgy for ultralow carbon and automobile grade of steels to reduce Carbon pick-up from refractory body to liquid steel. Even as alternative to other C-free refractories, the newly developed alumina-spinel fired brick is another superior generation fired refractory for achieving high performance in highly corrosive metallurgical environment (such as C/A 1-1.5, CaF_2 up to 5%, $MnO_2 \approx 2\%$). Such Alumina Spinel brick is manufactured by using proper granulometry of high purity synthetic alumina aggregate (Tabular alumina or white fused alumina or mixed), non-stoichiometric Mag-Al spinel in finer fractions and calcined alumina in matrix. The present work describes the effect of alumina aggregate on product properties such as density, porosity, shrinkage, cold and hot strengths as well as on the application properties such as abrasion, slag corrosion, thermal spalling which are of prime focus of end users for evaluating refractories for predicting higher performances. SEM studies and pore size distributions are analyzed to understand the roles of aggregate materials on properties. It is seen in industrial applications that refractory lining life has increased with Alumina-Spinel lining compared to previously used MgO-C lining due to better resistances to abrasion and corrosion. Although the cost of refractory lining has increased compared to traditional MgO-C linings, however the overall cost of refractory per ton of liquid steel for the steel plant has reduced due to higher lining life in metal zone. The present paper describes the usefulness of this newly developed fired alumina-spinel refractory in terms of refractory manufacturing (i.e. formulations and property evaluations) as well as steel shop application (i.e. application and performance).

INTRODUCTION

Steel ladle refractories evolved many stages of changes over last several decades. Till mid of 1990s, fired high alumina refractories with significant amount of silicates (e.g. andalusite or bauxite) were used in the metal zone of steel ladle lining. They could not perform well in contact with corrosive calcium aluminate slag because of high wear. The next developments were the era of graphite containing refractories (e.g. magnesia-graphite or alumina-magnesia-graphite) where non-wettability of graphite was the primary aspect to incorporate in refractories. However, high quality steel demand called for reduction or elimination of graphite present there. This demand was strengthened by the development of increasing requirements of special grade steels (e.g. ultralow carbon steel, alloy steels, interstitial-free steel etc) for automobile and other industries where low concentration targets of S, P, O, N, H, C etc in steel [1] are essential. To cater to these demands, some process changes were also made in steel metallurgy. The first change was in steel metallurgical process with addition of various secondary treatments [2,3] like vacuum degassing (e.g. RHD). This change has also resulted very severe process parameters for refractories such as increased residence time, higher tapping temperature, very corrosive slag etc. In the late 1990s, further development was established in secondary steelmaking area for advanced clean steel production in the form of alumina-spinel monolithics lining [4]. The primary need behind such innovation was to cater the growing need of advanced metallurgy for ultralow carbon and automobile grade of steels to reduce C-pickup from refractory to liquid steel. The monolithics concept was well supported by endless lining idea. However, in absence of monolithic ladle lining concept and limited ULC or IF grade steel production, alumina-spinel fired brick is an alternative superior refractory for achieving high performance (means higher productivity in steel making shop supported by performance predictability) in highly corrosive metallurgical environment. Alumina-rich Mag-Al spinel is used to impart significant advantages of slag penetration and corrosion resistance as well as spalling resistance. Alumina-rich non-stoichiometric Mag-Al pre-reacted spinel has the capability to absorb FeO or MnO from corrosive calcium aluminate slag within the free vacancies in its crystal structure. Thus slag becomes more viscous and this retards slag infiltration in refractories. Additionally, excess CaO available in slag reacts with Al_2O_3 in refractories to make thin layer of CA_6 in the interface of slag and refractories. This works as protective layer over refractories and helps in slag penetration resistance. It is also well established that purity of such alumina-spinel refractory plays vital role in the performance [5] and suitable quantity of spinel improve the wear mechanism by improving corrosion and spalling resistances [6,7,8]. Certainly to achieve this, proper quality of spinel addition in terms of size grading is also an essential aspect [9,10]. The recent development of alumina-spinel fired brick made it suitable to meet the refractory demands where steel ladle metal zone can withstand very aggressive slag attack and stay thermodynamically stable in contact with clean steel metallurgy [11]. In addition to this, the C-free refractory also helps to overcome energy loss problem and other operational factors arising due to high thermal conductivity of graphite bearing refractory lining.

The prime raw materials for fired alumina-spinel brick are aggregate alumina, mag-al spinel, calcined alumina and organic temporary binder. Such aggregate alumina and mag-al spinel materials are manufactured by synthetic routes but can be either sintered or fused in nature. The present paper describes comparative evaluation of refractories made from sintered and fused manufacturing routes of alumina aggregate. However, the effects of spinel manufacturing (sintered or fused) and other parameters like selections of granulometry, type of matrix alumina, refractory production parameters etc are not part of this paper. The evaluation of laboratory refractory blocks were done for different physicochemical properties like, porosity, density, strengths, expansion/ shrinkage, spalling, corrosion, abrasion etc. On the outset, the objective of such work was to see the effect of sintered Tabular alumina and white fused alumina in the refractory properties so as to predict the performance of such refractories in application.

EXPERIMENTAL

To restrict other oxide impurities at a very low level, all the raw materials of this type of alumina-spinel refractories are synthetic in nature. The selected raw materials are different commercially available size fractions of white fused alumina (WFA), tabular alumina (TA) and sintered mag-al spinel (SS78) and mentioned with the chemical properties in Table 1 and physical properties in Table.2. Calcined alumina is the matrix part of such refractory and a pure α-alumina of mono-modal PSD with specific surface area (BET) of about 1.0 m^2/g and d50 of about 3.4 µm is selected. The matrix part is also constitutes of spinel as it is distributed only in fine fractions so as to impart optimum corrosion resistance. Commercially available organic binder is used for the green shaping and providing drying strength.

Tab.1: Typical chemical analysis of selected raw materials

	Na_2O %	Fe_2O_3 %	SiO_2 %	MgO %	CaO %	Al_2O_3 %
TA	0.28	0.03	0.02	<0.01	0.02	99.65
WFA	0.31	0.03	0.03	<0.01	0.02	99.60
SS78	0.09	0.16	0.04	21.76	0.20	77.74
Cal. Al_2O_3	0.11	0.02	0.02	<0.01	0.02	99.8

Tab.2: Typical physical properties of selected raw materials

	Water Absorption%	Open porosity %	BSG g/cc
TA	0.8	1.5	3.60
WFA	2.2	5.2	3.71
SS78	0.47	1.5	3.26

Majority of refractory properties depend on the properties of raw materials mentioned on Tab.1 and Tab.2. However, the grain size distribution of materials selected in a formulation also play very significant role to optimize the final properties of the refractory. In order to find such optimum grain size distribution, initially, optimum packing density of mixes made out of combination of commercially available different size fractions of only Tabular alumina was checked. At first 100% Tabular Alumina, produced from sintered processing route, based formulation and its grain size distribution was selected (100T78B). Then, to understand the effect of alumina aggregate from different manufacturing route, white fused alumina was introduced in the formulation in step wise addition of 25% by replacing Tabular alumina. In this way, formulation 0T78B was designed with 100% WFA. The Tab.3 indicates the formulations selected. At this designing stage, the overall volumetric particle size distribution of the dry alumina mix was matched in each formulation because TA and WFA have differences among BSG, distribution in grain size distribution of few size fractions and particle shape. Thus, it was found that to control the mix grain size volumetric distribution of the mix at similar trend, amount of particular fraction of WFA vary with the amount of TA in same fraction in different formulations. As grain toughness and reactivity of TA and WFA are different among these synthetically produced α-alumina aggregates and there is also grain shape difference between TA and WFA, thus the particle packing of the mixes with TA and WFA are bit different as well. The formulation is shown in Table.3.

Similar experimentation with sintered spinel and fused spinel is also conducted but could not be shared and discussed here due to space constrain.

Tab.3: Mix formulation of different combinations

	100T78B	75T78B	50T78B	25T78B	0T78B
TA 1-3mm	35	18	4	-	-
WFA 1-3mm	--	17	34	38	39
TA 0.5-1mm	14	14	10	--	--
WFA 0.5-1mm	--	--	--	12	12
TA 0-0.5mm	11	11	14	10	-
WFA 0-0.5mm	-	-	-	2	10
TA 0-0.2mm	8	8	6	6	-
WFA 100mesh	-	-	-	-	5
WFA 325mesh	-	-	-	-	2
SS78 0-0.5mm	9	9	9	9	9
SS78 -45µm	13	13	13	13	13
Calcined Al_2O_3	10	10	10	10	10

RESULTS AND DISCUSSION

Cube of 50×50×50mm size and rectangular bars of 25x25x150mm size were prepared using pressure of ≈170MPa. These were first dried at 110°C for 24 hours and then fired at 1680°C with 2 hours soaking time. These blocks and bars were checked for density, porosity, compressive and flexural strengths. High temperature flexural strength (HMOR) was checked both at 1450°C and 1500°C with 30 minutes soaking time. Thermal shock was evaluated by air quenching method for checking spalling resistance. The samples were heated up to 1200°C, kept at that temperature for 10 minutes, then quenched to room temperature for 10 minutes and again inserted into the furnace. The residual flexural strength (MOR) of the samples after 5 such thermal spalling cycles was measured. Firing shrinkage was measured w.r.t green sample dimension and repeat PLC (PLCR) was measured on re-fired samples at 1700°C for 2 hours soaking. The abradability index was checked where 14lbs of BFA grains of 0.7-1.7mm size were injected at 45º inclined direction and weight loss was indexed as per Morgan Marshall method. X-ray diffraction (XRD) and SEM of selected samples were compared. The results of the conducted tests are discussed here. However, induction furnace slag corrosion test is planned and will be shared later.

The very first and foremost characteristic of refractories for working lining is its porosity. It also indirectly guides the densification and strength as well as resistances to spalling and corrosion. Fig.1 shows porosity trend of different formulations to indicate the effect of aggregate on porosity.

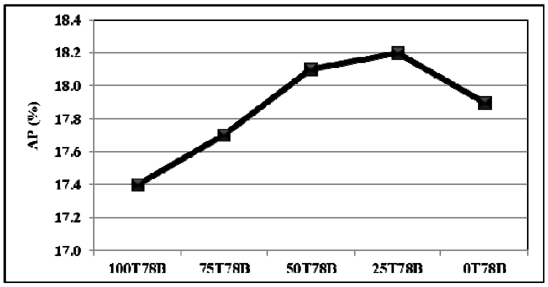

Fig. 1: Effect of sintered and fused aggregates on porosity

It is seen from Fig.1 that apparent porosity of the batches increases as TA was stage wise replaced by WFA. This has happened in spite of adjustments in overall mix PSD made of 2 different alumina aggregates. The increasing trend of porosity continues till 75% addition of WFA. However, in case of 100% WFA, possibly the grain shape difference also played an effect and improved porosity by helping in compaction. Fig.2 indicates the effect of different white aggregates in density and strength development. Addition of WFA into the mixes increased bulk density in all cases. This is quite obvious as WFA has higher BSG than that of TA. It is interesting to find that the effect of TA and WFA on porosity and density do not follow conventional reverse relationship. As there is significant difference among TA and WFA in particle shape (affecting particle packing) and reactivity (affecting sintering behaviour), so porosity is lower in 100% TA batch in spite of lower green and fired density. The higher sinter reactivity in sintered aggregate TA compared to fused aggregate WFA of higher inertness has resulted this difference in porosity. Such difference is also quite prominent in strength differences and 75-100% TA containing batches showed much higher CCS than rest batches with higher WFA proportions.

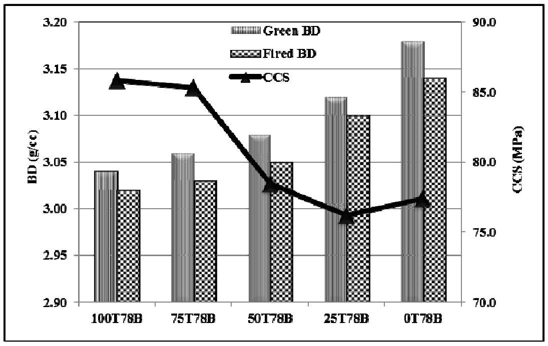

Fig. 2: Effect of aggregates on density and strength

Similar trend of compressive strength was observed in bending strength too and the effect of higher sinter reactivity of TA over WFA was also seen in case of cold MOR. The 100% WFA containing batch showed a marginal increase of CCS and MOR compared to the trend. However, in case of cold MOR after thermal spalling cycles, that trend didn't persist (Fig.3). Here, a continuous fall in MOR was observed in spalled samples. With increasing WFA%, the MOR drop% also increased. This could be explained by the aggregate microstructure analysis in Fig.4 where it is seen that TA is having well distributed and small closed pores but large open pores are visible in WFA. The presence of these micropores act as crack inhibitors in TA containing body and imparted better thermal shock resistance than WFA containing body which has large open pores and lesser number of closed pores.

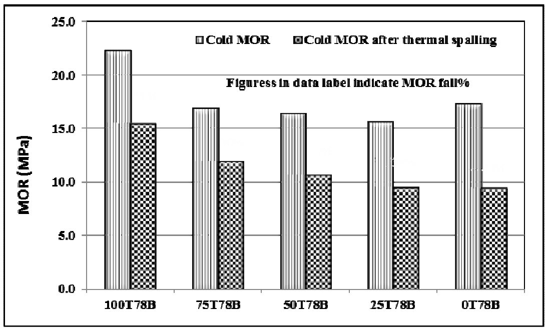

Fig. 3: Cold MOR – before and after thermal spalling

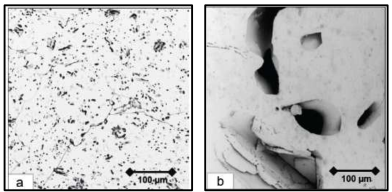

Fig. 4: Microstructure of TA (left) and WFA (right)

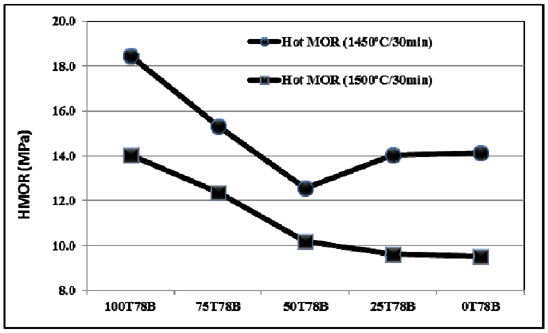

Fig. 5: Effect of aggregates on hot MOR

Fig.5 explains high temperature strength differences in the batches. 100% TA containing batch showed much higher hot MOR as compared to other samples mainly due to inhomogeneity in the distribution of chemical impurities especially in fines fraction. A marginal increase in hot strength for 100% WFA containing batch is probably due to improved grain interlocking within materials of same nature of grain shape. However, HMOR of 100% WFA batch is still significantly lower than that of 100% TA containing batch. This grain shape effect was completely nullified during testing HMOR at 1500ºC. HMOR at 1500ºC had dropped for all the batches compared to 1450ºC but still remained higher with 100% TA containing batch. The better compactness during sintering and higher chemical purity played advantageous role for higher amounts of TA containing batches (100T78B and 75T78B).

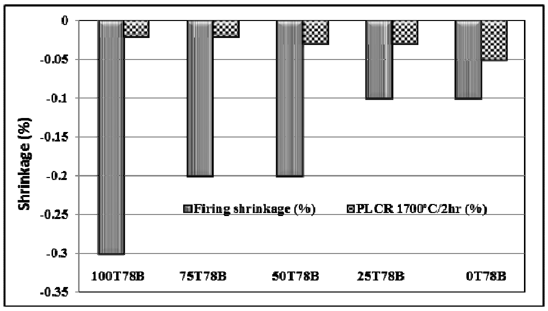

Fig. 6: Effect of aggregates on shrinkages during firing

Fig.6 explains the shrinkage behavior during initial and repeat firing. Significant difference in behavior observed among 100% TA vs 75-100% WFA containing batches whereas 50-75% TA containing batches behave similarly. This clearly indicates the reactivity vs inertness among these 2 different aggregates in same firing conditions. TA being more thermal reactive in nature, showed major shrinkage in 1st firing (PLC) and left with lower residual shrinkage for 2nd firing (PLCR). However, WFA being relatively inert in nature, showed lower shrinkage in 1st firing (PLC) but left with further higher shrinkage in 2nd firing (PLCR) compared to TA containing batches. This difference could be very significant for deciding mould dimension as the impact of aggregate switching had shown substantial effect on final fired brick dimension control.

The abrasion resistance behaviour is also showing similar pattern (Fig. 7). Lower the value of abradability index better is the abrasion resistance. In this respect, 100% TA containing sample has the highest resistance to abrasion. Incorporation of WFA reduces the resistance to abrasion. The brittle fused grains were displaced giving rise to generation of new surface in WFA containing batch whereas sintered Tabular grains having tougher and unique microstructure exhibit higher abrasion resistance index. The particle shape difference also supports this outcome. WFA grains has low roundness (means splintery in nature) as derived from aspect ratio analysis and thus commonly used in abrasive industry where the purpose is to cut the other body by dislodging own grains. However, TA with higher aspect ratio (means more cubic in nature) exhibit better abrasion resistance property.

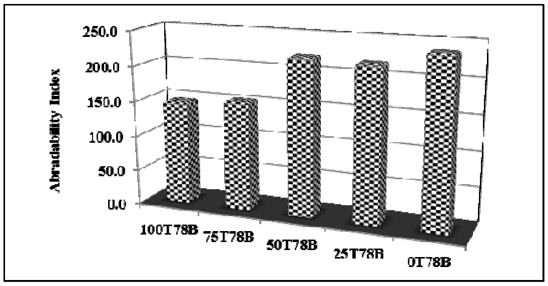

Fig. 7: Effect of aggregate type on abradability index

Alumina-spinel fired brick are used in steel ladle metal zone mainly and slag corrosion resistance is not the primary test which is essential to evaluate property of such brick. However, any change of aggregate can affect the slag penetration behavior and thus induction furnace slag corrosion test is planned and the findings will be presented later. It is good to remember that TA is produced in sintered route and possess much lower average pore diameter (0.7µm) compared to WFA produced in fusion route possessing much higher average pore size diameter (43.9µm). Tests conducted as per DIN66133 indicates (Fig.8) that 100% TA containing body is supposed to prevent slag penetration significantly than in 100% WFA containing body.

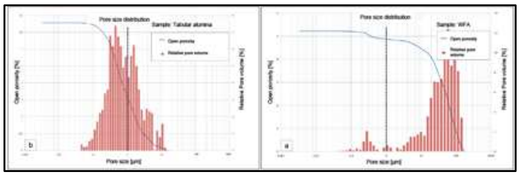

Fig. 8: Pore size distribution of TA (left) and WFA (right)

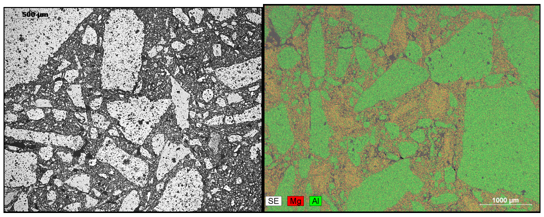

Fig. 9: Stereo microscopy and SEM-EDX of 100T78B

The best combination of evaluated properties were achieved for 100% TA containing batch 100T78B and checked for stereomicroscopy and SEM-EDX. Fig.9 explains well embedded TA grains with equally distributed spinel in matrix. Corundum and Spinel are main phases (Fig.10) which exhibited high thermo-mechanical properties and there is no significant minor phase noticed.

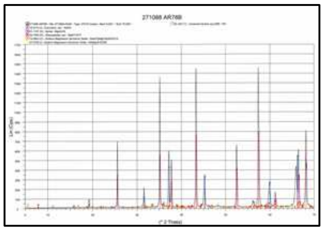

Fig. 10: XRD of 100T78B

ALUMINA-SPINEL BRICK - INDUSTRIAL USAGE

Newly developed fired Alumina-Spinel refractory is used successfully in LD2 and LD3 shops of Tata Steel Jamshedpur in India for lining in 165 ton steel ladle. The process routes involve 60-70% LF in Al-killing metallurgy with partial RH degasser and Ca-treatment. The tapping temperature is in the range of 1640-1650ºC with average holding time of 90 mints (LD2) and 120 mints (LD3). In place of earlier MgO-C lining, the newly developed brick shows potential of 25% higher service life with higher production share of IF grade steel of severe metallurgy. The additional benefits achieved are uniformity in erosion pattern, better adherence and consistency to target life, better shop environment (reduction in fume generation during preheating) and saving of energy (reduction in tap temperature, lesser outer shell temperature, less% of re-heating etc).

CONCLUSION

Tabular alumina containing body shows lower porosity and higher compressive and bending strengths due to higher sinter reactivity and typical microstructure in spite of lower density to WFA body whose thermal spalling resistance is worse due to absence of microporous with closed porosity. Abrasion resistance is better with TA body due to grain toughness and grain shape advantage. Hot strength and volume stability is higher with TA over WFA due to homogeneity and consistency in impurities and controlled sinter reactivity of TA. Fired Alumina-Spinel lining helped to increase shop floor confidence significantly.

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