DEVELOPMENT OF Al_2O_3 – $MgAl_2O_4$ SPINEL CASTABLE FOR VARIOUS APPLICATIONS

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ABSTRACT

To fulfill the needs from automobile industry, ultra-low carbon (ULC) and interstitial-free (IF) grades of steel are getting more importance. The stringent specification of steel can be fulfilled not only the special secondary metallurgical process but also the performance reliability of refractory lining in different equipment. The performance of refractory lining depends on operational safety, life, specific refractory cost along with its contribution for achieving the high demanding metallurgical targets where interaction of steel and refractory plays a vital role.

Al_2O_3 – $MgAl_2O_4$ castable is a special grade of castable used in different areas as working lining like steel ladle as well as in different prefabricated refractory items like well block, seating block, porous plug, RH snorkel etc. The application areas are very stringent and therefore high temperature thermo-mechanical properties are very important along with slag corrosion resistance. Spinel is one of the base raw materials, but the type of spinels and its grain size distribution are important while designing this castable.

In the present work, one special spinel is incorporated in the matrix which not only gives the excellent slag corrosion resistance but also have better thermal spalling resistance, volume stability and high temperature thermo-mechanical properties like HMOR and RUL. In presence of special material there is enough formation of CA_6 which enhance the volume stability and other properties. This castable is used to make seating block and well block for steel ladles and the performance is enhanced significantly.

INTRODUCTION

The growing interest to use spinel containing castables either in different pre-fabricated (PCPF) items or as monolithic lining is related to improve the performance, reduce the application cost and time. Due to the high corrosion resistance to basic slag, either pre-formed or in situ spinel containing refractory castables are nowadays widely used in steel ladle linings.

In 1990s, a second group of spinel castables was developed. Instead of pre-reacted spinel, these castables contain free magnesia in the matrix fines, which form spinel by reacting with alumina during use at high temperatures[1-4]. Spinel forming castables have shown advantages when compared to spinel containing ones in steel ladle side wall lining and have become a common material for this region in the past 20 years. For other applications like well block, seating block, purging plugs, spinel containing castables are advantageous and have become the standard one.

Preformed spinel is added to alumina castables for two major purposes. One is to increase the slag corrosion resistance and other one is to improve the thermo-mechanical properties. The spinel containing castables show less penetration and less corrosion when compared to the pure alumina against basic and acidic slag compositions[5]. The optimal spinel content is in the range of 15 – 30 wt%, preferably between 20 and 25 wt%. If too little spinel is added, it results in a higher corrosion rate whereas if there is too much spinel, it leads to high penetration because the spinel does not react with the infiltration slag[6].

Another important aspect is the grain size distribution of the spinel. Spinel must be added predominantly to the fine fraction of the castable formulation to attain the best penetration resistance[7]. Spinel addition enhances the thermal shock resistance of alumina castables which can be explained by the different thermal expansion cooefficient between alumina and spinel. The different expansion leads to microcracks in the matrix act as crack branchers when the material is thermally stressed[8].

Another way to design spinel castables is in-situ while introducing fine magnesia and alumina in matrix. The use of magnesia, as one of the reactants for the spinel formation in castables, often causes difficulties such as poor flow or quick setting due to the magnesia hydration. Furthermore, the volume expansion owing to the hydration may lead cracking during the drying step, which is practically critical when producing pre-cast shapes. For "in situ" spinel forming castable a theoretical volume expansion[9] is 8% while forming spinel between Al_2O_3 and MgO. Apart from volume expansion several micro cracks are generated which lead to better thermal spalling resistance. But one of the disadvantage for "in situ" spinel forming castable is the hydration of MgO as it is added in very fine forms. A special care must be taken to control the hydration of MgO as well as the associated expansion. An excessive expansion while forming in situ spinel is also not expected. The volume expansion due to the in situ spinel formation can close joints at the surface. Therefore, castables with spinel formation provide advantages in ladle side walls.

Effect of CAC cement in spinel containing castable (30% spinel) was studied[10] and it has been observed that increasing CAC content influenced the sinterability and strength. The slag penetration decreased while increasing CAC content to a certain extent. Presence of different phases in CAC cement like CA, CA_2 and CA_6 form a dense barrier and reduce the slag penetration. It has also observed[11] that the slag corrosion resistance of spinel castable is more effective when spinel is added in medium and fine fraction rather than coarse aggregate.

The special features for spinel containing castables are (a) excellent slag corrosion resistance (b) high mechanical strength (c) volume and structural stability at application temperature (d) good thermal shock resistance (e) reduce tendency for crack formation in application and (f) limited infiltration of slag at high temperature.

In steel ladle bottom and especially for purging plugs, seating blocks and well blocks, the volumetric stability under high temperature and pressure is most important. High erosion resistance and thermal shock resistance are also important during intensive stirring of the steel and when cold stirring gas is blown. Spinel containing castables have become the standard for this application and provided the best performance.

In this present work, one new Al_2O_3-$MgAl_2O_4$ castable has been designed while introducing a special material in matrix having dual purpose. It gives better slag corrosion resistance as the super fine spinel particles are uniformly distributed in matrix and thus prevent slag corrosion. At the same time this material is having CA and CA_2 phases exhibiting hydraulic properties.

EXPERIMENTAL

A new castable is designed with pre-formed spinel along with a special material used in matrix. The main objective was to improve the slag corrosion resistance, thermal spalling resistance and volume stability during application. This castable was specifically designed for precast items like well block, seating block, porous plugs etc. All the relevant properties like flow decay, AP, CCS, PLC, thermal spalling resistance along with thermo-mechanical propertues like HMOR were measured. AP and CCS were measured after drying as well as after firing the samples at 800^0C, 1100^0C, 1500^0C and 1600^0C. Repeat PLC was measured at 1600^0C with five cycles. Slag corrosion test was carried out in induction furnace with two different types of slag of basicity 3.5 and 2.1 at 1600^0C. All properties are compared with the regular Al_2O_3 – Spinel castable to understand the improvement. With the improved material, well block and seating blocks were manufactured and tried in integrated steel plants. The performance of the improved material was monitored and compared with regular spinel castable.

RESULTS AND DISCUSSIONS

In regular castable pre-formed spinel is used in the range of 25 – 30%. For better performance two types of spinels were used in regular castable. One is alumina-rich spinel A and other is alumina-rich spinel B.

Table I : Formulation of regular and trial castable

Formulation	Existing	Trial
Synthetic Alumina	55	a
Alumina Rich Spinel A	10	b
Alumina Rich Spinel B	20	c
Reactive Alumina	10	10
CA Cement	5	Nil
Special material	Nil	y
Dispersant	x	x

Most of the spinels were used in matrix along with some amount in coarse fraction. In Table I the formulation of regular castable and trial castable is shown. In trial castable, special material was used in matrix and there was no cement as the special material is having the properties of cement. Though the special material was used, to meet the chemical properties, some amount of other pre-formed spinels were also used.

For sample preparation, 4.8% water was added for regular as well as trial recipe. The self flow and flow decay was measured upto 90 minutes. The behaviour of flow decay is shown in Fig 1. In case of trial recipe the flow is better than regular one. Not only flow, the working time is also more for trial recipe.

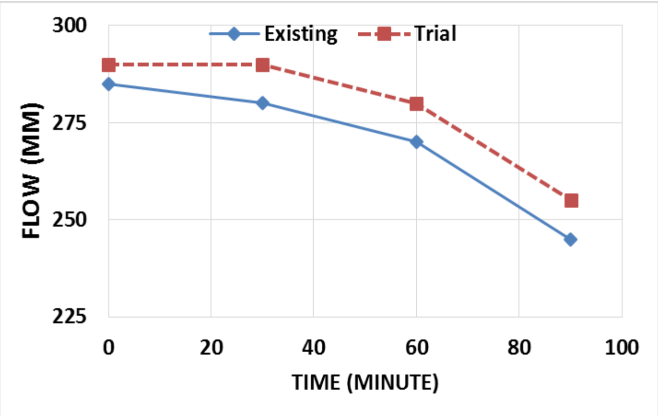

Fig. 1. Flow decay of castable

AP values are mentioned in Fig. 2 and it is observed that the trial material is showing lower AP after drying as well as after firing at different temperatures. Though the water added was same but the trial material is having diffeent grain size distribution along with higher maximum grain. Due to revised grain size distribution AP is low in trial material.

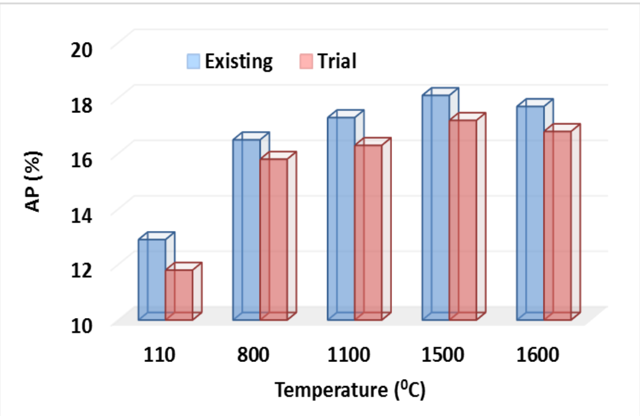

Fig. 2. AP for regular and trial castables

Measurement of CCS is very important as the trial material does not have any cement. In case of trial material the CCS has come from special material only. But interestingly, CCS of trial material is in the same range after drying and after firing at different temperatures as shown in Fig. 3.

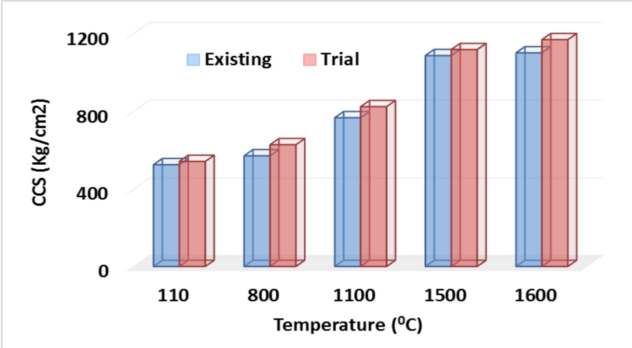

Fig. 3. CCS for regular and trial castables

HMOR was measured at 1400^0C and 1500^0C and shown in Fig. 4. Before measurement HMOR, the samples were pre-fired at the corresponding temperatures with three hours soaking. There is improvement in HMOR both at 1400^0C and 1500^0C for trial material. This may be due to design of trial material without cement. Of course the CaO content in both the cases is almost same.

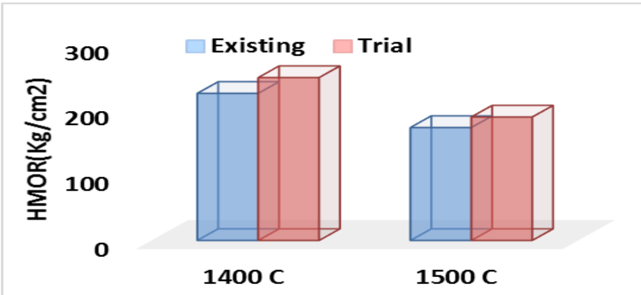

Fig. 4. HMOR of regular and trial castables

This castable is designed specifically for well block, seating block, porous plugs etc. where volume stability is very important. To understand the changes in volume, PLC was measured at 1600^0C with repeated cycle upto five cycles and shown in Fig. 5 for regular castable and in Fig. 6 for trial castable.

In repeat PLC there is significant change in regular and trial castable. In case of regular castable initially the PLC is positive but in next cycle it became almost zero and subsequently there is shrinkage. But in trial castable the magnitude of positive PLC is small but there is almost same PLC upto fifth cycles. This behaviour in trial material indicates it is having better volume stability which will help to prevent crack formation during application.

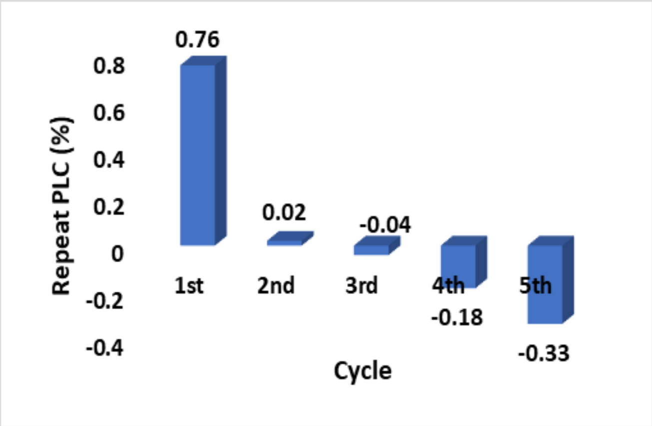

Fig. 5. Repeat PLC for regular castables

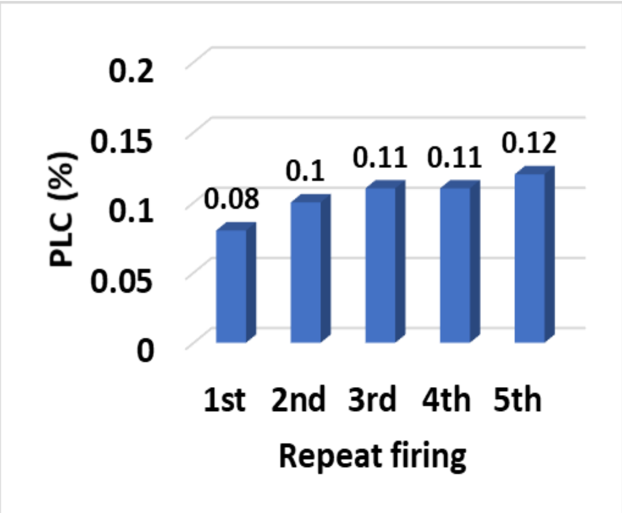

Fig. 6. Repeat PLC for trial castables

Fig. 7. Appearance of samples after 25 cycles (Left : Regular castable, Right – Trial castable)

Thermal spalling resistance was measured from 1300^{0}C to water quenching with a sample of size 50 mm dia and 50 mm height. After 25 cycles (Fig. 7), the regular castable was disintegrated into several pieces whereas the trial castable was in a good condition except one small crack formation. Ultimately the trial castable was disintegrated after 64 cycles as shown in Fig. 8. This behaviour of trial material supports that it is having better thermal spalling resistance than regular one.

Fig. 8. Disintigration of trial castable after 64 cycles

Slag corrosion test was conducted at 1600^{0}C in induction furnace with two different slags of basicity 3.5 and 2.1. The slag chemistry is shown in Table II.

Against both slags the trial castable is having better slag corrosion resistance. The improvement is ~ 23% in terms of corrosion depth. The penetration is negligible in both the cases.

Table II : Chemical analysis of slag

Slag Type	A	B
Slag chemistry	% by wt.	% by wt.
CaO	53	31.6
FeO	19	43.5
MnO	6	0.62
SiO_2	15	15.5
MgO	5	2.4
Al_2O_3	2	6.2
C/S	3.5	2.1

With trial castable, well block and seating block were manufactured to take plant trial in an integrated steel plan. The ladle capacity for this plant is 300 MT. The finished seating blocks and well blocks manufactured with trial castable is shown in Fig. 9 and Fig. 10.

One of the main issues with regular castable was cracking in blocks resulting unwanted outage and it was difficult to predict about the performance of ladle. The cracking of seating blocks is shown in Fig. 11.

Fig. 9. Seating block for 300 MT steel ladle

Fig. 10. Well block for 300 MT steel ladle

Fig. 11. Cracking observed in seating blocks with regular castable

The appearance of trial blocks after different life (heats) of blocks was observed against the regular one to understand about the formation of crack. In Fig. 12 and in Fig. 13, the appearance of blocks is shown after 26 heats and after 48 heats. In regular castable, cracking was observed even before 26 heats and it enlarged to a large extent with subsequent heats. But in trial block there was no cracks even after 48 heats.

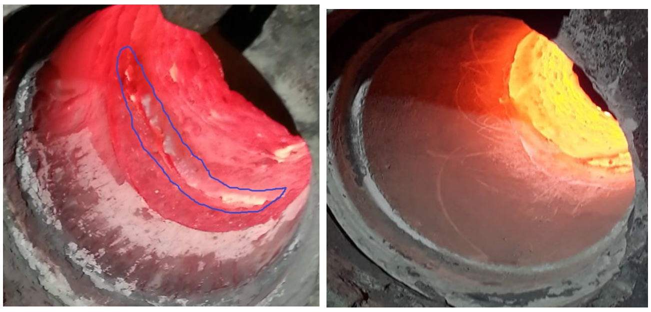

Fig. 12. Appearance of blocks after 26 heats (Left : Regular castable, Right – Trial castable)

Fig. 13. Appearance of blocks after 48 heats (Left : Regular castable, Right – Trial castable)

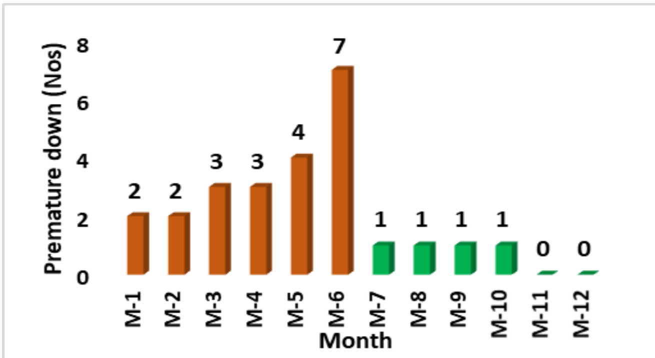

Fig. 14. Unwanted outage of ladle due to cracking of seating blocks

The trial castable is having better thermal spalling resiatance from its designing view point as this castable consists of revised grain size distribution along with large maximum grain, introduction of special material in matrix and also reinforcement with metallic fiber. All those changes help to prevent cracking during application.

The unwanted outage of ladle was also reduced significantly after using trial blocks. In Fig. 14, numbers of unwanted outages is shown before and after use of trial seating blocks. From M-7 (month – 7), trial blocks were used and outage was reduced to one for first four months. In last two months unwanted outage is zero whereas before using trial block the average monthly unwanted outage was ~ 3.5 times with the maximum of 7 in M-6.

The overall life of the seating blocks with trial castable is also improved as the erosion rate is reduced significantly.

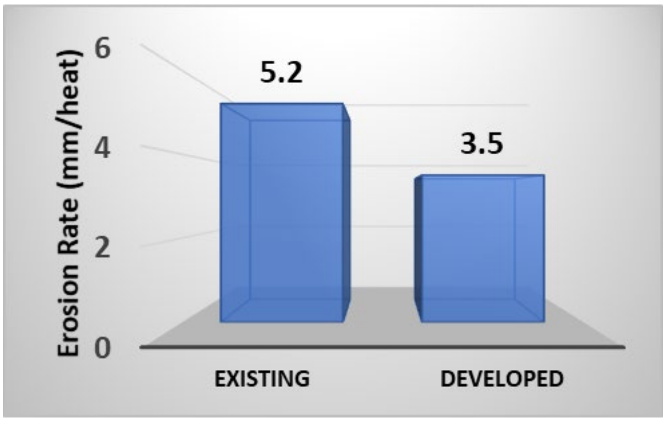

Fig. 15. Height – wise erosion rate of blocks

In Fig. 15 and Fig. 16, erosion rate along the height and bore is shown both for regular castable and trial castable.

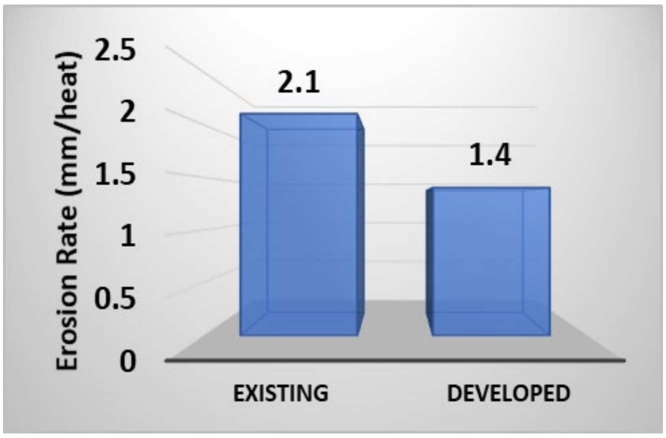

Fig. 16. Inside bore – wise erosion rate of blocks

The individual performance of first 27 nos of seating blocks is shown in Fig – 17 with the average heats of 47.8 and maximum heat is 64. In case of regular blocks the average life was 42.2 heats. Apart from average life the major improvement is to eliminate cracks during operation to avoid unwanted outage of ladle.

This integrated steel plant is now switched over to 100% trial blocks. Now this plant has started to use well blocks also, with this trial castable and getting similar improved performance.

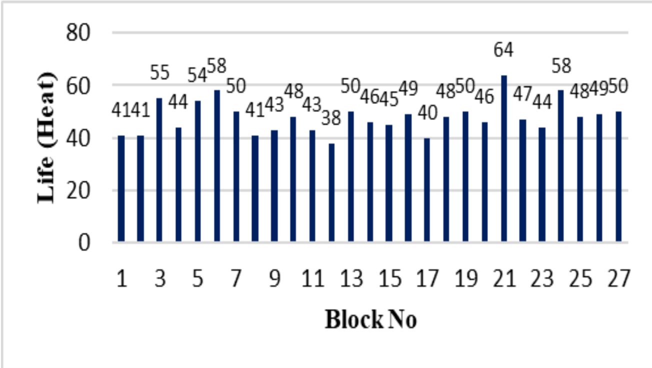

Fig. 17. Individual seating block life (Heats)

CONCLUSIONS

Cracking of seating block and well blocks during operation is serious issue as it causes unwanted outage of steel ladle. To overcome this issue, one new castable in Al_2O_3 – $MgAl_2O_4$ route is designed while introducing special material in matrix, revised the grain size distribution along with increasing the maxium grain size and reinforced with metallic fiber. There is significant improvement in thermal spalling and slag corrosion resistance. This castable is showing positive PLC with repeat firing at 1600^0C indicates better volume stability. Other thermo-mechanical properties like HMOR is also improved. This improved castable was used to manufacture both seating block and well block for plant trials. The performance for both the blocks is improved significantly not only in terms of heats but also reduce the cracks significantly, resulting reduction in unwanted outages. The trial is now extended to other steel plants and similar improvement in performance is observed. In next step, the same castable will be tried for porous plugs and RH snorkel for better performance.

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