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An efficient $MgAl_2O_4$ spinel additive for improved slag erosion and penetration resistance of high-Al_2O_3 and MgO–C refractories

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Abstract

A stoichiometric dense $MgAl_2O_4$ spinel has been prepared according to a conventional double stage firing process using $AlCl_3$ as a sintering aid. A stoichiometric mixture of aluminum trihydroxide and caustic MgO was calcined at 1300 °C for 1 h in order to achieve a desired degree of spinelization. $AlCl_3$ in different amounts, i.e. 0.911, 1.822 and 2.733 wt.%, was coated on spinelized powder using wet-impregnation technique and sintered at different temperatures ranging from 1500 to 1600 °C for 1 h. Among the spinels sintered at 1550 °C for 1 h, spinel incorporated with 2.733 wt% $AlCl_3$ has exhibited superior properties in terms of bulk density, apparent porosity and water absorption. Further, this sintered stoichiometric spinel incorporated with 2.733 wt.% $AlCl_3$ was characterized by means of scanning electron microscopy (SEM), energy dispersive analysis with X-rays (EDAX) and electron probe microanalysis (EPMA). EDAX analysis revealed that $AlCl_3$ as a sintering aid helps in reducing the Na_2O present in the raw materials composition after sintering. EPMA studies revealed that spinel prepared in this study is well comparable with the commercial spinel (Alcoa, AR-78, USA). Finally, 20 wt.% of the stoichiometric spinel incorporated with 2.733 wt.% $AlCl_3$ prior to sintering was added to high-Al_2O_3 and MgO–C refractories to evaluate its effect on slag erosion and penetration resistance as well as on repeated permanent linear change (PLC) of these bricks. By the addition of stoichiometric $MgAl_2O_4$ spinel, the slag erosion and penetration resistance of high Al_2O_3 and MgO–C refractories was improved remarkably, and their PLCs exhibited more steady and stable positive values after spinel addition.

Keywords: $MgAl_2O_4$; $AlCl_3$; High Al_2O_3; MgO–C; Slag erosion; Slag penetration; Permanent linear change; EPMA

1. Introduction

Magnesium aluminate spinel has been recognized as one of the effective refractory materials and used in various applications such as steel ladles, cement rotary kilns, vacuum induction furnaces, continuous casting tundishes, degasser snorkels and lances, glass industries, etc. [1,2]. $MgAl_2O_4$ spinel possesses high-melting point, high chemical inertness against both acidic and basic slags, low expansion values at elevated temperatures, and is an ecologically benign refractory material [3,4]. Various grades of magnesium-aluminate spinels are available in the market with different alumina and magnesia contents. Generally, MgO-spinel bricks are preferred for cement rotary kilns whereas Al_2O_3-spinel castables are preferred for steel laddles [3–6]. The lifetimes of linings made of high purity alumina and magnesia-carbons are limited by their high wear rates arising from slag penetration and structural spalling. Recently, castables made of high alumina incorporated with spinel have been found to show good performance in steel ladles as sidewall as well as bottom along with MgO–C bricks containing spinel grains in slag line [7,8]. Furthermore, these castables have been proven to be the most cost-effective lining to meet severe service conditions in steel making [9]. Thus, stoichiometric $MgAl_2O_4$ spinels associated with high alumina and magnesia-carbon bricks are proven to be the best refractories.

In spite of many advantages, production of $MgAl_2O_4$ spinel as a refractory material involves rather an expensive

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processing route. This is mainly because of volume expansion of about 8% [10], which occurs during $MgAl_2O_4$ spinel formation from its constituents alumina and magnesia. On account of this expansion it is difficult to obtain a dense $MgAl_2O_4$ spinel body in a single stage firing process. In order to overcome this volume expansion problem, an intermediate calcination step has been introduced in the preparation of dense $MgAl_2O_4$ spinel [11]. In this process, first the raw materials have been calcined at around 1400 °C to get an appreciable amount of spinel phase and then sintered into a dense body. However, these high calcination temperatures not only impede the formation of dense spinel bodies, but also results in higher processing costs. There are some mineralizers (e.g. AlF_3, V_2O_5, Y_2O_3, NaCl, $MgCl_2$, etc.) which promote the formation of spinel and thus, can reduce the calcination temperatures [12,13], which in turn reduces the cost of the production. Despite this, in most of the cases, the spinel so obtained has a low reactivity and requires higher sintering temperatures (>1650 °C) to form a dense product. Some additives (e.g. TiO_2, B_2O_3, ZnO, Fe_2O_3, CaO, etc.) have also been identified to reduce the sintering temperatures of $MgAl_2O_4$ spinel [14–16]. Nevertheless, these additives inevitably contaminate the product and restrict its application to lower temperatures. In a previous paper, $AlCl_3$ was identified as an effective sintering aid when added to optimum spinelized powder (calcined at 1300 °C for 1 h) [17] results in an improved sintered density of up to 96% at 1550 °C for 1 h devoid of any contamination.

In the present study, a stoichiometric $MgAl_2O_4$ spinel was prepared using $AlCl_3$ as a sintering aid and was further characterized with the help of both spectroscopic and non-spectroscopic techniques including EPMA, SEM, EDAX, and XRD. Finally, an attempt was made to explore the effect of stoichiometric $MgAl_2O_4$ spinel produced in the present process as an additive on the slag erosion and penetration resistance, and also on the permanent linear change of high alumina and magnesia–carbon refractories.

2. Experimental procedure

2.1. Raw materials used

Commercial aluminum trihydroxide (Nalco, NSPH-10, India) made according to the Bayer process, was used as the alumina raw material and caustic MgO (Birla Periclase, India), made from sea water magnesia, was used as the magnesia raw materials for making $MgAl_2O_4$ spinel. Their physico-chemical properties are listed in Table 1. Aluminum chloride (Loba Chemie, AR Grade, India) was used as a mineralizer. The steel ladle slag (Vishakapatnam Steel Plant, India) was used to evaluate the slag erosion and penetration resistance of bricks used in the present study.

Table 1
Physical properties and chemical composition of raw materials

Material	$Al(OH)_3$	Caustic MgO
Al_2O_3 (wt.%)	64.5	–
MgO (wt.%)	–	82.86
Na_2O (wt.%)	0.3	0.093
CaO (wt.%)	0.03	0.908
SiO_2 (wt.%)	0.009	0.97
Fe_2O_3 (wt.%)	0.007	0.106
LOI (RT-1000 °C)	34.5	15.5
Specific gravity (g/cc)	2.42	3.58
Average particle size (μm)	85	5.22

2.2. Material preparation and characterization

A stoichiometric $MgAl_2O_4$ spinel was prepared following a typical double stage firing process described elsewhere [17]. A stoichiometric mixture of aluminum trihydroxide and caustic MgO were first calcined at 1300 °C for 1 h. Calcined spinel powder was impregnated with different amounts of $AlCl_3$ and then sintered at various temperatures ranging from 1550 to 1650 °C for 1 h. Spinels sintered at 1550 °C for 1 h in the presence of 0, 0.01, 0.02 and 0.03 mol% (0, 0.911, 1.822 and 2.733 wt.%, respectively) $AlCl_3$ are designated as MAS0, MAS1, MAS2 and MAS3, respectively. Bulk density, apparent porosity and water absorption of spinels so obtained were measured according to Archimedes principle using a Mettler balance with attachment (AG 245, Mettler Toledo, Switzerland).

Phase analysis of the samples were carried out by X-ray diffraction (Bruker D8 advanced system) using Cu-$K\alpha$ radiation. Relative phase compositions of samples were calculated from the peak height measurements for the respective peaks. The change in lattice parameter 'a' of the cubic $MgAl_2O_4$ phase in the fired sample was determined from the characteristics XRD lines of the $MgAl_2O_4$ spinel phase using NBS ADIS *83 computer programme supplied by ICDD. The microstructure of dense spinel grains was examined using scanning electron microscope (JSM-5410, Jeol, Japan) with an energy dispersive scanning (Sigma 3.42 Quaser, Kevex, USA) attachment for qualitative and quantitative micro analysis. The MAS3 sample was analyzed by electron probe microanalysis (EPMA, Model Cameca SX 50) after mounting it on araldite platform, chemically etched (phosphoric acid at 185±5 °C for 4 min), polished and gold coated for conductivity. For the purpose of comparison, a commercially available high purity spinel material (Alcoa, MAS 76, USA, specification: Al_2O_3–78%; MgO–22–23%; CaO–0.22–0.26%; SiO_2–0.08–0.12; Na_2O–0.06–0.12%; Fe_2O_3–0.06–0.09; bulk density

3.25–3.29 g/cc, apparent porosity 1.5–2.0% and water absorption 0.4–0.6%) was also used in EPMA analysis. EPMA analysis was done by three methods namely line scan analysis, spectrum analysis and image analysis.

2.3. Slag erosion and penetration as well as PLC tests

Around 3 kg of MAS3 was crushed into 259–600 μm size powders and added to high alumina and magnesia-carbon bricks prepared according to methods of Korgul et al. [8], and Robin, et al. [18], respectively. In this study, four sets of refractory bricks, [namely: high–alumina (70% Al_2O_3, Chinese bauxite based), high-alumina + 20 wt.% MAS3 spinel, magnesia–carbon (Chinese fused magnesia based) and magnesia–carbon + 20 wt.% MAS3 spinel bricks], were prepared having the sizes of 80×80×65 mm each and provided with the hole of 44 mm diameter and 35 mm depth in the centre of the piece. Chemical compositions and physical properties of these refractory bricks are listed in Table 2. Standard methods of slag erosion (cup test, JIS R 2214, Japan and DIN 1069, Germany) and slag penetration (IS 1528 part IV, 1974) were adopted to test these bricks.

For each test, ∼50 grams of slag (∼600 μm) was placed in the test piece cavity and heated to 1650 °C for 2 h in an electrical furnace. Chemical composition of the slag is given in the Table 3. During heating, precaution was taken to avoid oxidation of magnesia–carbon bricks by placing the bricks in saggers filled with coke breeze of 3–6 mm size fraction. The bricks were taken out from the furnace and cooled to room temperature. The cooled samples were then cut vertically along the center of the cavity. In order to evaluate the extent of slag erosion and penetration, 10 different locations along the diameter (side-wall) and 5 locations along the depth (bottom) were taken and averaged out.

Table 2
Chemical composition and physical properties of high Al_2O_3 and MgO–C bricks

Materials	Property
(a) MgO–C bricks	
MgO (wt.%) on loss free basis (Chinese fused magnesia based)	97
Fixed carbon including anti-oxidants (wt.%)	9
Bulk density (g/cc)	3–3.5
Apparent porosity (%)	3–4
Cold crushing strength (MPa)	0.4
(b) High alumina bricks	
Al_2O_3 (wt.%), (Chinese bauxite based)	>70
Fe_2O_3 (wt.%)	>1.5
Bulk density (g/cc)	2.8
Apparent porosity (%)	18–21
Cold crushing strength (MPa)	0.5

Table 3
Composition of test slag

Composition	Wt.%
CaO	50.7
MgO	8.0
FeO	21.0
SiO_2	15.9
Al_2O_3	0.5
MnO	4.4
CaO/SiO_2	3.1
$CaO + MgO/SiO_2$	3.69

3. Results and discussion

3.1. Densification behaviour of the spinel

It is well documented in the literature that partially spinelized (70–80%) powders can be sintered into a high dense spinel body as compared to fully spinelized or un-calcined powder at elevated temperatures [11,12,17]. Since, the process of complete spinelization requires higher calcination temperature as compared to partial spinelization, higher calcination temperatures always leads to the formation of hard agglomerates which in turn results into poor sintering of the spinel body. It is a well-known phenomenon that un-calcined powders can not be sintered into a dense spinel body because of volume expansion associated with the spinel formation [10]. In this study, a stoichiometric mixture of aluminum tri-hydroxide and caustic MgO was calcined at 1300 °C for 1 h in order to achieve spinelization of around 80% (conformed by XRD analysis) [10]. Our previous study has clearly indicated that $AlCl_3$ is more effective as a sintering aid in improving the sintered properties of stoichiometric $MgAl_2O_4$ spinel, when it is added to partially spinelized powder (75–80%) instead of to the fully spinelized powder or to the raw materials prior to the calcination. The possible role of $AlCl_3$ as a sintering aid in improving the densification properties of stoichiometric $MgAl_2O_4$ spinel has already been discussed elsewhere [17]. In the literature, Bakker and Lindsay [12] reported that AlF_3 (1–3 wt.%) is also an effective mineralizer to improve the spinelization of aluminum hydroxide and magnesium hydroxide on calcination at 1400 °C and up to 97% theoretical density can be achieved at 1600 °C. Aluminum halides when added to the raw mixture prior to calcination accelerate the gamma→alpha transition in alumina. They also promote the crystal growth of alpha alumina during calcination [19]. During firing aluminum halides pyrohydrolyze to alumina and gaseous hydrogen halides and hence, do not contaminate the product.

X-ray diffraction patterns of $MgAl_2O_4$ spinel prepared with out any sintering aid (MAS0) and with the addition of 2.733 wt.% $AlCl_3$ (MAS3) confirmed only the presence of $MgAl_2O_4$ spinel phase and complete absence of un-reacted phases of periclase or corundum. This indicates that there is a complete formation of spinel solid solution in both the samples MAS0 and MAS3 after sintering at 1600 and 1550 °C, respectively, for 1 h. The stoichiometry of both the spinel samples (MAS 0 and MAS 3), were confirmed from their corresponding lattice parameters calculated by adopting the standard experimental procedure. MAS0 and MAS3 spinels prepared in the present investigation exhibit the lattice parameters of 8.069 and 8.070 Å, respectively. These values are well comparable with the results reported recently for stoichiometric spinel bodies [20]. Thus, these values indicate that both the spinels (MAS0 and MAS3) exist in stoichiometric composition.

Stoichiometric $MgAl_2O_4$ spinels sintered at 1550 °C for 1 h in the presence of $AlCl_3$ as a sintering aid were characterized for their bulk density, apparent porosity and water absorption as shown in Fig. 1 as a function of $AlCl_3$ content. In general, the bulk density of spinel increases with the sintering temperature irrespective of $AlCl_3$ content, and as a result the apparent porosity and water absorption values would decrease. As can be seen from Fig. 1, as the amount of $AlCl_3$ increases, bulk density of $MgAl_2O_4$ spinel is also increased and the apparent porosity and water absorption values are decreased as noted as a function of sintering temperature. It is interesting to note that 2.733 wt.% $AlCl_3$ is sufficient to sinter the stoichiometric $MgAl_2O_4$ spinel with appreciable density when it is added to partially "spinelized" (82%) powder. The enhanced sintering in the presence of $AlCl_3$ as a sintering aid is confirmed by SEM micrograph of fractured surface depicted in Fig. 2 [17].

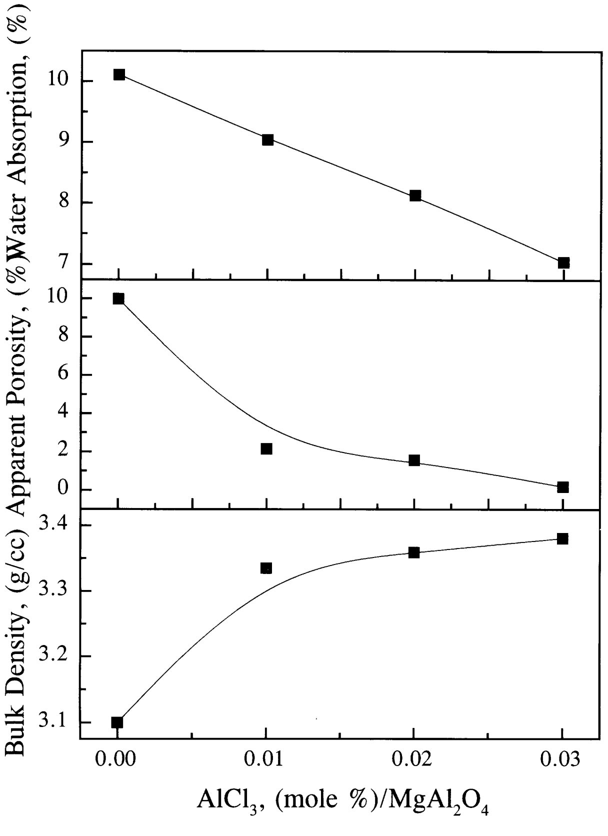


Fig. 1. Variation of bulk density, apparent porosity and water absorption of sintered magnesium aluminate spinel at 1550 °C for 1 h as a function of the amount of $AlCl_3$.

3.2. Analysis of EDAX and EPMA

The EDAX spectrum of stoichiometric $MgAl_2O_4$ spinel prepared in the presence of $AlCl_3$ (MAS 3) and with out $AlCl_3$ (MAS 0) are shown in Fig. 3a and b, respectively. As can be seen from Fig. 3a, there are no peaks corresponding to chloride and sodium, however, Fig. 3b clearly shows the presence of peaks due to Na_2O. Probably, the presence of chlorine may assist in the evaporation of Na_2O which is one of the harmful impurities, by forming NaCl (melting point, 800 °C; boiling point, 1465 °C [21]) during sintering of $MgAl_2O_4$ spinel in the presence of $AlCl_3$ at above 1550 °C [17]. This is an added advantage for using $AlCl_3$ as a sintering aid.

According to EPMA line scan analysis of MAS3 sample, a drastic decrease of both Al and Mg counts near the grain boundaries and a variation of Al (~9000) and Mg (~4000) counts even within the grains were observed during analysis. The corresponding line scan analysis profile is given in Fig. 4, indicating that the investigated sample is not uniform with respect to its constituents throughout the specimen. X-ray spectrums recorded on suitably tuned crystals of MAS3 and AR-78 (Alcoa) samples are shown in Fig. 5a and b, respectively. As can be noted from these figures only Mg and Al are present as major elements along with some small traces of Si, Fe, and P. Though the starting materials of

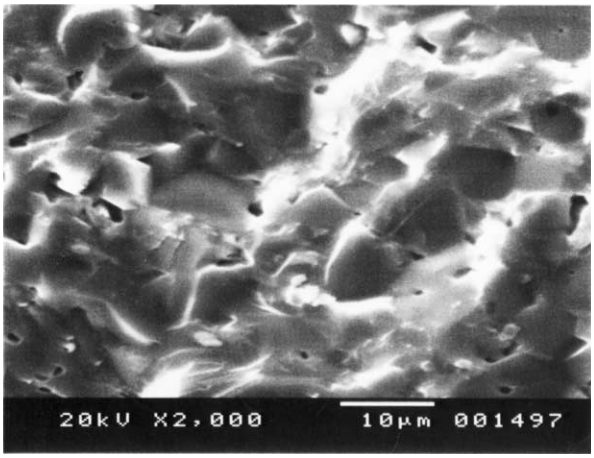
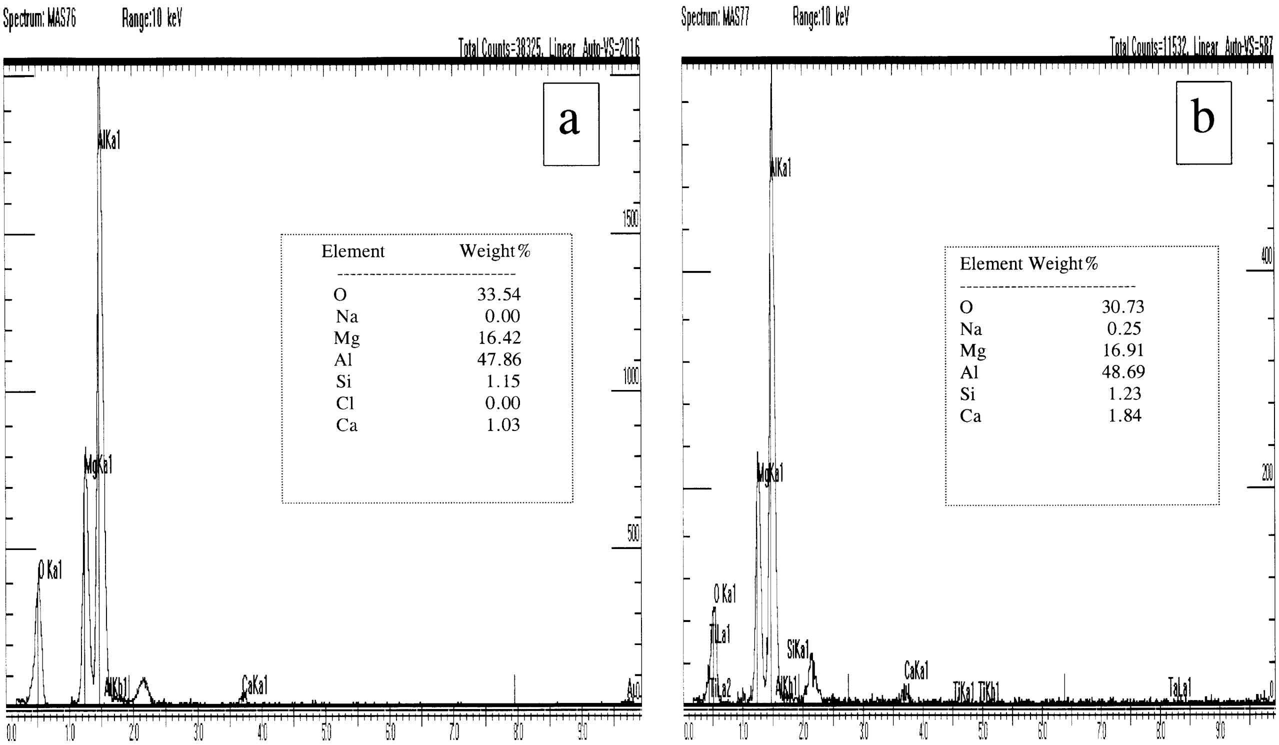


Fig. 2. Scanning electron micrograph of fractured surface of sintered magnesium aluminate spinel at 1550 °C for 1 h in the presence of 2.733 wt.% $AlCl_3$ (MAS3).



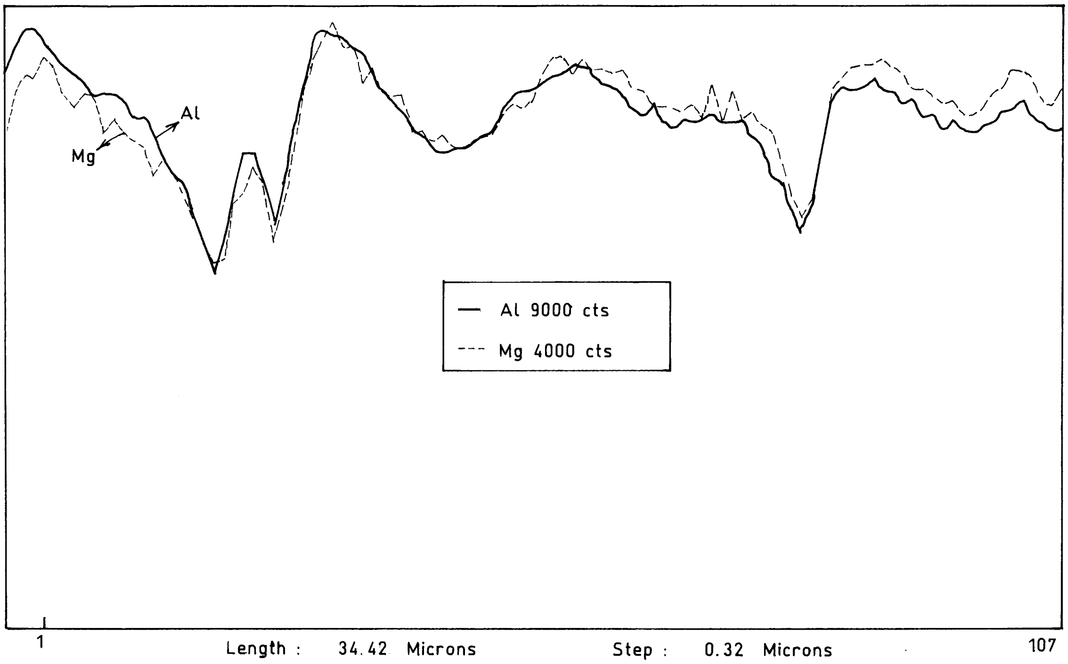
(a)

Element	Weight%
O	33.54
Na	0.00
Mg	16.42
Al	47.86
Si	1.15
Cl	0.00
Ca	1.03

(b)

Element	Weight%
O	30.73
Na	0.25
Mg	16.91
Al	48.69
Si	1.23
Ca	1.84

Fig. 3. Energy dispersive analysis with X-rays of sintered magnesium aluminate spinel at 1550 °C for 1 h in the presence of 2.733 wt.% $AlCl_3$ (MAS3) (a) and in the absence of $AlCl_3$ (b).



Length : 34.42 Microns Step : 0.32 Microns

Fisrt point coordinates : 11940 830 -122 Counting time : 1000 ms

Last point coordinates : 11940 830 -122

Fig. 4. EPMA line scan analysis of sintered magnesium aluminate spinel at 1550 °C for 1 h in the presence of 2.733 wt.% $AlCl_3$ (MAS3).

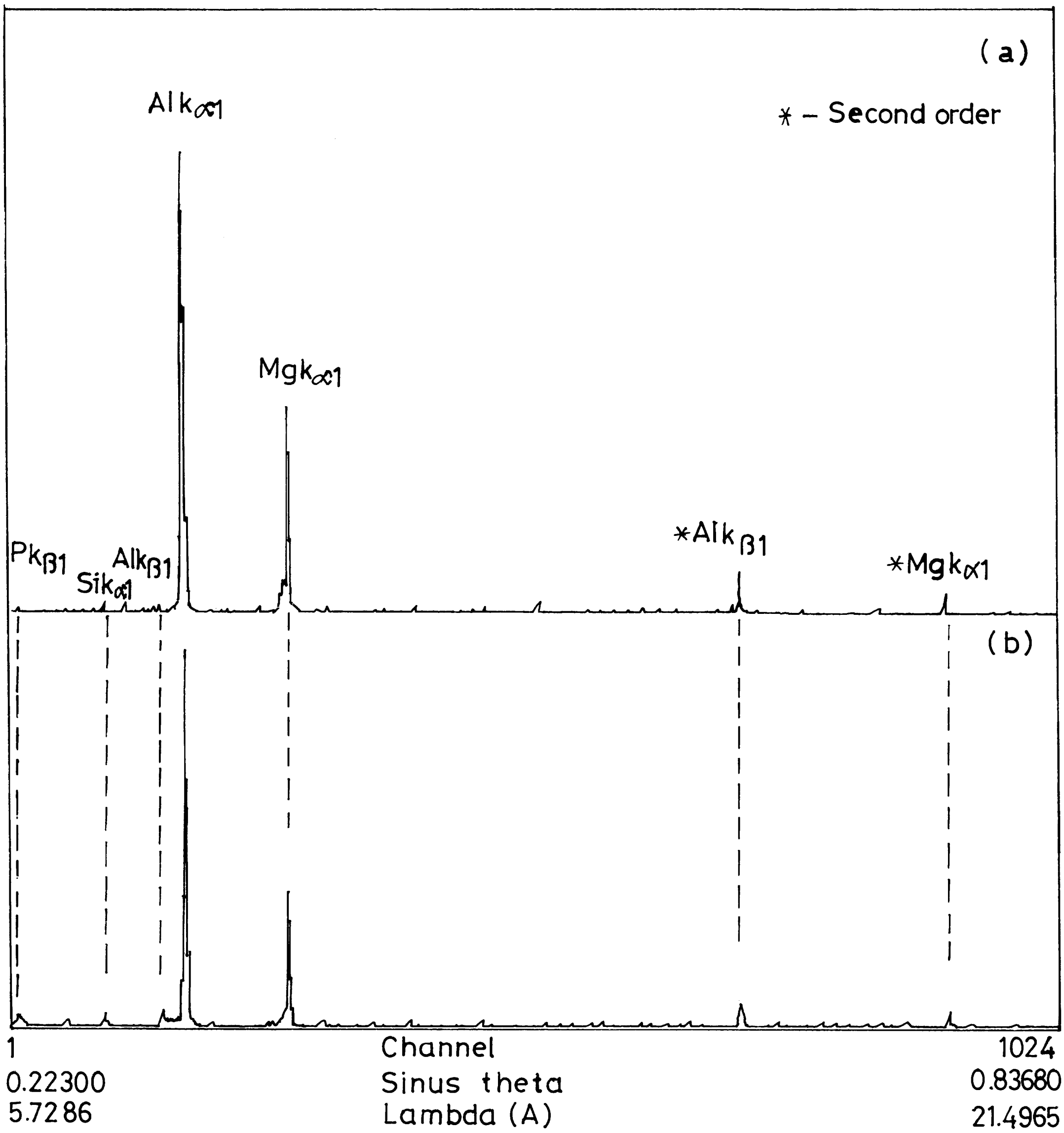


Fig. 5. X-ray spectrum of sintered magnesium aluminate spinel at 1550 °C for 1 h in the presence of 2.733 wt.% $AlCl_3$ (MAS3) (a) and magnesium aluminate spinel Alcoa, AR-78 (b).

MAS 3 contain impurities such as Na_2O, CaO, SiO_2, Fe_2O_3, etc. together ~3%, however, a low impurity content is observed from the spectrum (Fig. 4a) may probably be due to the leaching out of impurities at the grain boundaries during etching. Another interesting point to be seen from this study is that no chloride could be detected in the EPMA. Also, it is understood that both the samples are impurity free within the grains and $AlCl_3$ as a sintering aid does not contaminate the spinel product.

Secondary electron images of MAS3 and AR-78 spinels were viewed visually in order to measure the grain sizes. In MAS3, the grain sizes were found to vary between 2 and 10 μm and average grain size was found to be about 6 μm and in the case of AR-78, it was varying between 4 and 30 μm and average grain size was about 10 μm. This variation may be because of difference in their sintering temperature. There are probably two reasons for this observation of finer grains in MAS3 are; one is lower sintering temperature (1550 °C for 1 h) and another is $AlCl_3$ might be inhibiting the grain growth during sintering. Thus, EPMA analysis clearly indicated that MAS3 is well comparable with the Alcoa AR-78 spinel in all respects including bulk density, apparent porosity and water absorption values (Fig. 1 and Experimental).

3.3. Analysis of slag erosion and penetration as well as PLC

Slag erosion and slag penetration values of high-alumina along with 20 wt.% MAS3 spinel containing high-alumina, and magnesia–carbon along with 20 wt.% MAS3 spinel containing magnesia-carbons obtained by the tests conducted at 1650 °C for 2 h are shown in Fig. 6a and b, respectively. As can be viewed from these figures, when 20 wt.% MAS3 is added to high alumina and magnesia–carbon bricks, resistance to slag erosion and penetration are improved significantly. In the case of high alumina, the slag erosion resistance along the side wall (along the radius of the hole) and bottom (along the depth of the hole) are improved by 58.26 and 26%, respectively, and its slag penetration resistance also increased by 14.45%, after spinel addition. These results are well comparable with the results reported by Yamamura et al. [22] and Matsumoto et al. [23]. The improvement of slag erosion and penetration resistance after spinel addition to high alumina bricks is a well-known phenomenon [22–24].

Generally, stoichiometric $MgAl_2O_4$ spinel exhibits first deformation under 0.2 MPa at 2000 °C, does not react with silica until 1737 °C, CaO or MgO until 2000 °C and α-Al_2O_3 until 1927 °C, and can be used for all metals except alkaline earth [25]. Several authors, Matsumoto et al. [23] and Kurata et al. [24], suggested that the corrosion mechanism of alumina spinel refractories by a CaO–MnO–Al_2O_3–FeO/Fe_2O_3–SiO_2 slag is relatively simple. The CaO in the slag reacts with alumina in the refractory so that the slag becomes alumina-rich and precipitates low melting CaO–$2Al_2O_3$ and CaO–$6Al_2O_3$ products at the hot face. The refractory spinel, however, reacts with the slag MnO and FeO/Fe_2O_3 forming complex spinels, i.e. $(Mg, Mn, Fe)O \cdot (Fe, Al)_2O_3$. Deeper into the refractory, as the CaO and Al_2O_3 are used up forming CaO–$2Al_2O_3$ and CaO–$6Al_2O_3$ phases, the relative amount of silica increases to generate a high viscosity and high melting temperature slag which limits slag penetration [26]. This may be the probable reason in improving the slag erosion and penetration resistance of high alumina brick by the addition of $MgAl_2O_4$ spinel in the present case. In the case of MAS3 containing magnesia-carbon bricks, slag erosion resistance along the side-wall and bottom are improved by 47.72% and 45.31%, respectively. For magnesia–carbon bricks, it was difficult to measure the degree of slag penetration because of the black colour of the brick texture. The wear mechanism of spinel-carbon bricks has been deduced as follows [18b, 27]: first the oxidation of carbon occurs to some extent in the brick, then liquid steel and fused slag penetrates into the brick. Spinel can react with MnO, FeO in the slag to form solid solution, at the same time, the Al_2O_3 and SiO_2 of the brick react with the CaO in the slag to form gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) which has low melting point. This may prevent further slag penetration, resulting in improved slag resistance. A similar mechanism may be operative in the case of magnesia–carbon–spinel bricks as well.

Repeated permanent linear change (PLC) of high-alumina and 20% MAS3 incorporated high-alumina, and magnesia–carbon and 20% MAS3 incorporated

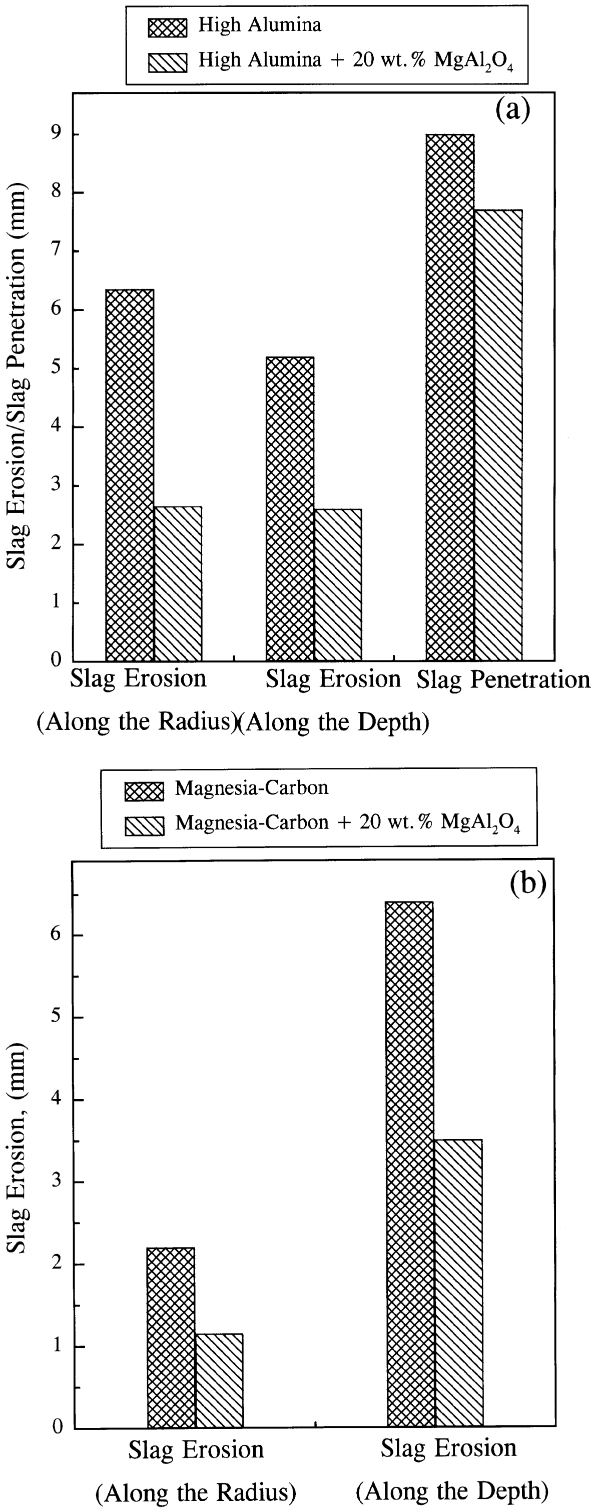


Fig. 6. (a) Slag erosion and penetration of high alumina and 20 wt.% MAS3 + high alumina bricks tested at 1650 °C for 2 h. (b). Slag erosion of magnesia–carbon and 20 wt.% MAS3 + magnesia–carbon tested at 1650 °C for 2 h.

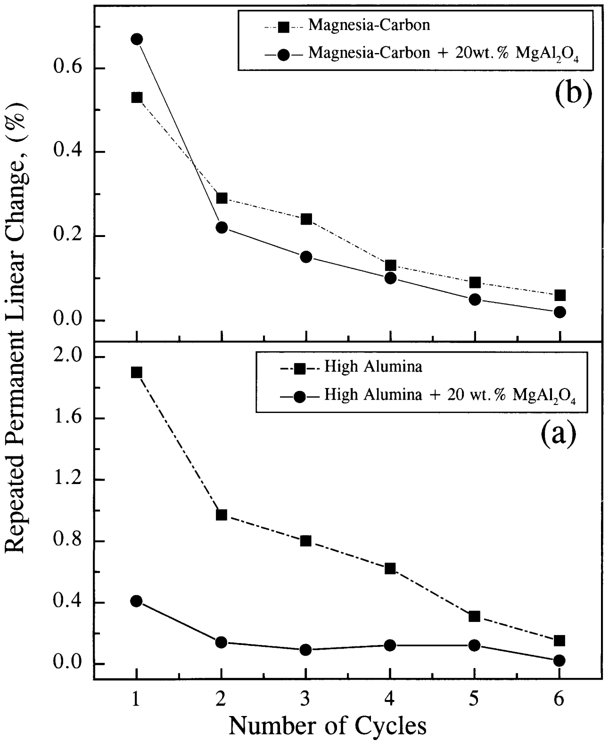


Fig. 7. (a) Repeated permanent linear change of high alumina and 20 wt.% MAS3 + high alumina bricks tested at 1650 °C for 2 h as a function of number of cycles. (b) Repeated permanent linear change of magnesia–carbon and 20 wt.% MAS3 + magnesia–carbon bricks tested at 1650 °C for 2 h as a function of number of cycles.

magnesia–carbon samples tested at 1650 °C for 2 h are given in Fig. 7a and b, respectively, as a function of number of cycles. As can be seen from Fig. 7a, 20% MAS3 incorporated high alumina exhibits more steady and stable positive PLC values when compared to pure high alumina test piece. However, in the case of magnesia–carbon bricks the addition of spinel does not show the similar improvement in PLC behaviour (Fig. 7b) as can be seen in the case of alumina brick (Fig. 7a). Though Fig. 7b appears to show the same trend of PLC values for both magnesia–carbon and spinel containing magnesia–carbon bricks for all the six cycles, a closer look would reveal that the incorporated spinel is having lesser thermal expansion as compared to its counter part. The relatively lower thermal expansion of spinel at elevated temperatures may be the reason for these beneficial PLC values.

4. Conclusions

1. In a double stage firing process, stoichiometric $MgAl_2O_4$ spinel can be sintered to a bulk density of 3.40 g/cc, apparent porosity of 0.193% and water absorption of 0.057% using $AlCl_3$ as a sintering additive at a relatively lower temperature of 1550 °C for 1 h.
2. A stoichiometric $MgAl_2O_4$ spinel prepared from aluminum trihydroxide and caustic MgO in the presence of $AlCl_3$ as an additive is well comparable with high purity spinel (Alcoa, AR-78, USA).
3. $MgAl_2O_4$ spinel as an additive improves the slag erosion and penetration resistance of high Al_2O_3 refractory by 58 and 14.5%, respectively, and slag erosion resistance of MgO–C refractory by 48%.
4. After $MgAl_2O_4$ spinel addition, both high Al_2O_3 and MgO–C refractories showed more steady and stable positive PLC values.

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