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Spinelisation and properties of Al_2O_3–$MgAl_2O_4$–C refractory: Effect of MgO and Al_2O_3 reactants

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Abstract

The effect of particle size of MgO and Al_2O_3 on the spinel formation associated with permanent linear change on reheating (PLCR) and microstructure of Al_2O_3–$MgAl_2O_4$–C refractory is investigated as a function of heating cycle at 1600 °C with 2 h holding at each cycle. It was found that rate of spinel formation and associated volume expansion is very much dependent on the reactivity and particle size of the reactant. When the reactants are very fine and reactive there is considerable amount of spinel formation, whereas coarser reactants with lower reactivity show negligible formation of spinel phase and associated expansion. Magnesia and alumina with moderate reactivity develops optimum PLCR of the refractory. It continuously increases with the number of heating cycles. The SEM photomicrographs show that in Al_2O_3–$MgAl_2O_4$–C refractory the spinel phase is formed in between the calcined bauxite grain and the EDX analysis indicates that the spinel phase formed is stoichiometric in nature.

Keywords: A. Sintering; C. Thermal expansion; E. Refractories; Spinel

1. Introduction

Carbon containing refractories such as MgO–C and Al_2O_3–C have been widely used for steel ladle lining. High alumina bricks give a lower life of steel ladle due to structural spalling. MgO–C and Al_2O_3–C bricks have negative or insufficient residual expansion causing joint erosion and corrosion of the lining. These refractories usually consist of more than 80 wt.% MgO/Al_2O_3, 10–15 wt.% graphite and few percent resin and antioxidant materials [1]. Due to rapid development of steel making process, there is a need of more precise match of refractory with the process condition and Al_2O_3–$MgAl_2O_4$–C bricks are getting the importance. Al_2O_3–$MgAl_2O_4$–C bricks have better performance over conventional high alumina and doloma refractory in steel ladle [2].

It was found that when unfired Al_2O_3–$MgAl_2O_4$–C refractories are heated at a temperature more than 1000 °C, magnesium aluminate spinel was formed by solid state reaction route. The spinel formation from its constituent oxides, i.e., MgO and Al_2O_3 is associated with a volume expansion of 5% [3,4], which leads to significant reduction in pore volume of the brick [5–7]. Due to this volume expansion Al_2O_3–$MgAl_2O_4$–C brick exhibits residual expansion during use, i.e., shows positive PLCR value. The expansion of the refractory results in monolithic lining which means a lower metal/slag infiltration and corrosion through brick joints [8,9]. The magnesium aluminate spinel possesses a good combination of physical and chemical properties. The better corrosion and thermal shock resistance of refractories have been reported to be influenced positively by presence of in situ spinel [10,11].

It was reported that spinel formation, with associated permanent expansion, was very much dependent on the kind and size of the reactant oxides [12]. The main objective of this work was to study the effect of particle size and reactivity of the spinel forming oxides on spinelisation and associated permanent linear change on repeated heating cycles. An optimum spinel forming batch was selected and used in the Al_2O_3–C composition to develop the Al_2O_3–$MgAl_2O_4$–C (AMC) refractories with improved microstructure and properties.

2. Experimental

The main raw materials used in this study to develop the spinel are magnesia both calcined and fused, tabular alumina

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and calcined alumina. Both fused magnesia and tabular alumina were crushed and ground to pass through −20 mesh BS sieve. All the raw materials are characterized in terms of chemical analysis and mineralogical phases. Batch composition utilizing different magnesia and alumina as shown in Table 1 were selected in such a way that the final batch contains 72% Al_2O_3 with respect to MgO:Al_2O_3 ratio. All the batch materials are uniformly mixed with 5% poly vinyl alcohol (PVA) solution as binder and uniaxially pressed into 0.6 cm × 0.6 cm × 6 cm bars under a pressure of 100 MPa. The green bars thus produced were first dried at 110 ± 5 °C and then heat treated at 1600 °C with 2 h holding time and cooled down to room temperature for three consecutive cycles. Heat treatment was done in a programme controlled furnace in oxidizing atmosphere and the heating rate was maintained at 5 °C/min up to 1000 °C and then 3 °C/min up to the final firing temperature. After each heat treatment their dimensional change was measured and phase analysis was done by XRD technique. The X-ray diffraction patterns of the finely powdered samples were obtained in a Philips X-ray diffractometer (Model PW 1730) using nickel filtered Cu Kα radiation and recorded over a Braggs' angle (2θ) range of 15–65°. From the results, an optimum spinel batch formulation was selected and used in the development of Al_2O_3–$MgAl_2O_4$–C refractory.

The Al_2O_3–$MgAl_2O_4$–C refractory was developed from calcined bauxite of different grain size, calcined alumina, fused magnesia, graphite and an antioxidant as per the composition given in Table 2 with resin as binder. Graphite was used at the level of 8% with 2 wt.% aluminium powder as antioxidant. The refractory blocks of dimension 7.5 cm × 7.5 cm × 7.5 cm were pressed under uniaxial pressure of 180 MPa and tempered at 180 °C for 24 h. Tempered blocks are then characterized in terms of bulk density, apparent porosity, cold crushing strength and PLCR at 1600 °C. Microstructural characterization was done by scanning electron microscopy (SEM) and elemental analysis by EDX. Bulk density and apparent porosity was determined by conventional liquid displacement method using Archimedes' principle. SEM was performed on the polished surface of AMC block after coking at 1600 °C. Coking of AMC block was done by embedding the sample inside graphite powder kept in an alumina crucible to maintain a reducing atmosphere and heat treated at 1600 °C for 2 h.

Table 1
Spinel forming batch composition.

Batch code	MgO source	Al_2O_3 source
FMTA	Fused magnesia	Tabular alumina
CMTA	Calcined magnesia	Tabular alumina
FMCA	Fused magnesia	Calcined alumina
CMCA	Calcined magnesia	Calcined alumina

Table 2
Batch composition of Al_2O_3–Mg-Al_2O_4–C refractory.

Components	%
Calcined bauxite	
2–6 mm	20.0
0.5–2 mm	40.0
0–0.5 mm	20.0
Calcined alumina	10.0
Fused magnesia	10.0
Graphite	8.0
Aluminium powder	2.0
Resin binder	4.0

3. Results and discussion

Chemical analysis of magnesia and alumina used to develop spinel is given in Table 3. All the raw materials are more than 97% pure. The crystalline phases present in alumina and magnesia are corundum and periclase, respectively. Both the calcined and fused magnesia contain the same amount of CaO as impurity.

Batches comprising different MgO and Al_2O_3 reactants are shown in Table 1. After heating these batches at 1600 °C for 2 h, the variation of PLCR value at different cycles is depicted in Fig. 1. It reveals that when both the reactants are coarser, i.e., fused magnesia and tabular alumina (FMTA), the expansion with increasing number of cycle is very low and when the reactants are finer and highly reactive (CMCA batch) the expansion in the first cycle itself is very high due to higher amount of spinel formation. The rate of expansion slowly diminishes in the subsequent heating cycles. XRD pattern of these samples after the first cycle is shown in Fig. 2. In the FMTA sample the spinel formation is almost inexistent and large peaks of MgO and Al_2O_3 are visible. The spinel formation for the CMCA sample is almost complete with the presence of very small amounts of unreacted Al_2O_3 and MgO. Other two compositions have moderate reactivity towards spinel formation. So the combination of tabular alumina and calcined magnesia (CMTA) and fused magnesia and calcined alumina (FMCA) are most suitable from the point of view of steady rate of expansion. Since calcined MgO has a hydration tendency, due to high surface area and low crystal size, fused magnesia and calcined alumina batch (FMCA) was used as spinel forming composition to develop the Al_2O_3–$MgAl_2O_4$–C refractory.

Table 3
Chemical analysis of spinel forming oxides.

Constituents (wt.%)	Tabular alumina	Calcined alumina	Fused magnesia	Calcined magnesia
Al_2O_3	99.5	99.3	0.2	0.3
Fe_2O_3	–	–	0.05	0.5
MgO	–	–	98.9	97.1
CaO	–	–	0.8	1.7
Na_2O	–	0.3	–	0.04

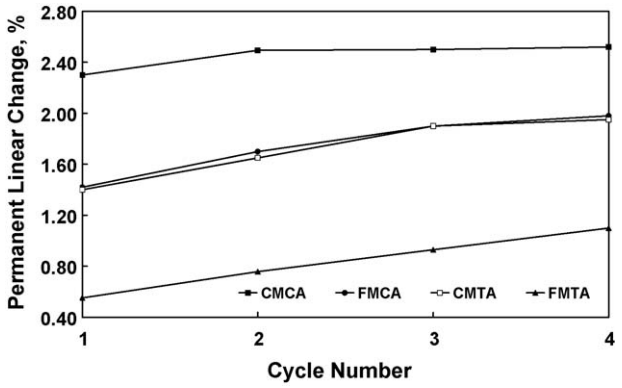

Fig. 1. PLC of different spinel compositions with the number of heating cycles at 1600 °C.

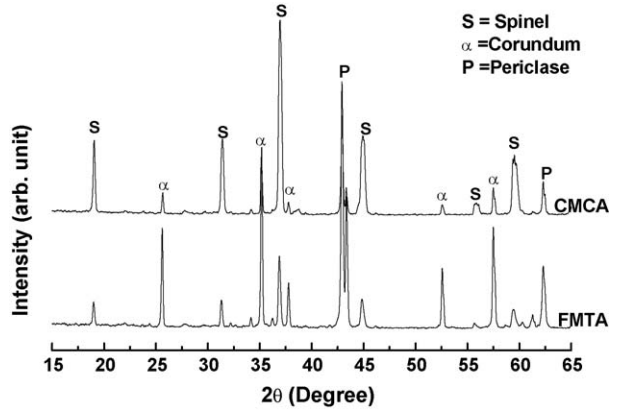

Fig. 2. XRD pattern of spinel composition after first heating cycle: (CMCA) calcined magnesia and calcined alumina and (FMTA) fused magnesia and tabular alumina.

The moderate reactivity of the FMCA batch will control the spinel formation on repeated heating and corresponding positive PLCR. Fig. 3 shows the phase development of FMCA batch on reheating at 1600 °C with number of heating cycles. It is observed that the amount of spinel formed is gradually increased with the number of heating cycle. The spinel formation even after the third cycle is not complete and there are some unreacted magnesia and alumina phases. This is the main reason for the controlled expansion of the FMCA sample as shown in Fig. 3.

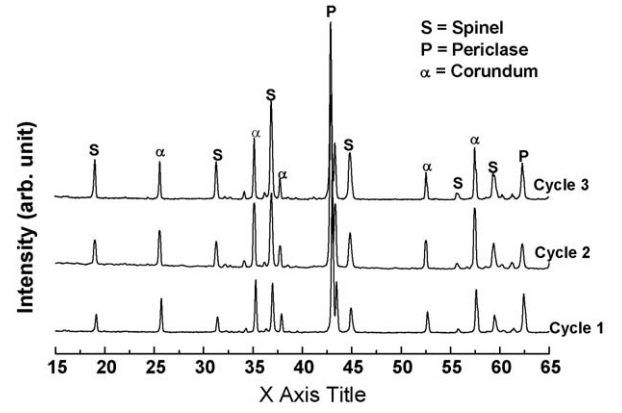

Fig. 3. Phase development of spinel composition containing fused magnesia and calcined alumina (FMCA) with number of heating cycle.

Table 4
Properties of Al_2O_3–Mg-Al_2O_4–C refractories.

Bulk density (g/cc)	3.09
Apparent porosity (%)	3.5
Coked bulk density (g/cc)	3.01
Coked apparent porosity (%)	11.5
Cold Crushing Strength (MPa)	50
PLCR at 1600 °C/2 h %	
First cycle	+1.50
Second cycle	+1.70
Third cycle	+1.95

The physical properties of the Al_2O_3–$MgAl_2O_4$–C refractory block developed using FMCA spinel composition and tempered at 180 °C is given in Table 4. The bulk density

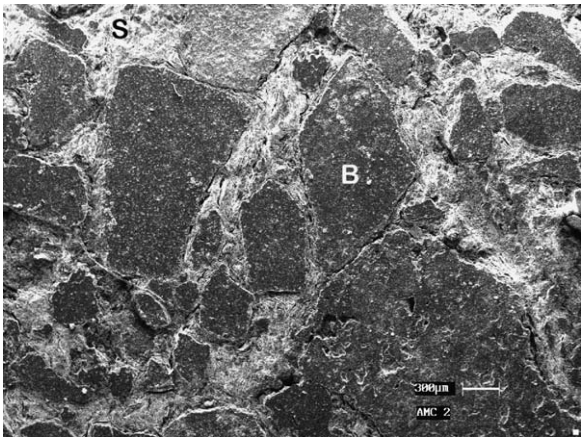

Fig. 4. SEM photomicrograph of Al_2O_3–$MgAl_2O_4$–C refractory block showing calcined bauxite grains (B) and intergranular spinel phase (S).

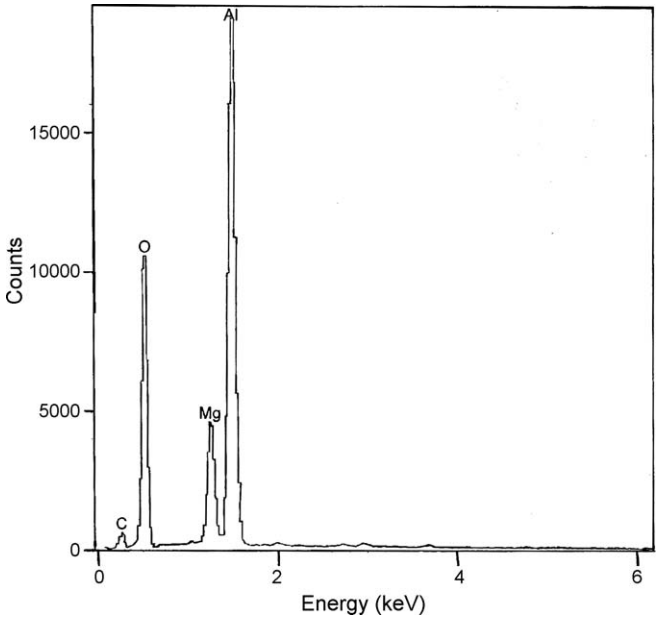

Fig. 5. EDX pattern of the white intergranular phase of Al_2O_3–$MgAl_2O_4$–C refractory.

and apparent porosity of the sample before and after coking show encouraging results. The cold crushing strength is as high as 50 MPa. The PLCR value after 3 heating cycles are +1.50%, +1.70% and +1.95%, respectively, which shows controlled spinel formation in the refractory.

SEM photomicrograph of the refractory block developed after coking is shown in Fig. 4., where calcined bauxite grains of different sizes are seen. It was observed that magnesium aluminate spinel (white phase) is distributed in the intergranular position. The in situ spinel acts as ceramic bond between the grains and control the PLCR of refractory. The EDX spectra of the white intergranular phase as shown in Fig. 5 indicate the formation of spinel at the grain boundary. Quantitative analysis reveals that the spinel formed is stoichiometric in nature.

4. Conclusions

Spinel formation is very much dependent on the particle size and reactivity of the starting magnesia and alumina. Spinel reactants with moderate reactivity give the optimum positive PLCR. Al_2O_3–$MgAl_2O_4$–C refractory block is developed with optimum PLCR at consecutive heating cycles, improved strength and lower coked porosity. Spinelisation and associated expansion (PLCR) were controlled by optimizing the particle size and reactivity of alumina and magnesia. Spinel composition from fused magnesia and calcined alumina shows optimum results. Microstructure and EDX analysis show that the spinel formation takes place in between alumina grains. The spinel acts as a bond between the grains, maintains the strength and controls the PLCR of the refractory and is stoichiometric in nature.

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