



Densification and properties of magnesia-rich magnesium-aluminate spinel derived from natural and synthetic raw materials

Somnath Sinhamahapatra, H.S. Tripathi, Arup Ghosh*

Refractory Division, CSIR-Central Glass & Ceramic Research Institute, 196, Raja S C Mullick Road, Kolkata, 700032 West Bengal, India

Received 27 August 2015; received in revised form 4 November 2015; accepted 7 December 2015

Available online 12 December 2015

Abstract

Magnesia rich magnesium aluminate spinel ($\text{MgO}:\text{Al}_2\text{O}_3=2:1$) was developed by reaction sintering of Indian natural magnesite of Salem region as well as from synthetic caustic magnesia with calcined alumina. Dilatometric study of the green compacts was carried out to evaluate the spinelisation and sintering behaviour of both the samples. Green samples were heat treated between 1400 to 1600 °C and characterised in terms of densification behaviour, high temperature flexural strength, microstructure and phase development. Spinel and periclase are the major phases in both the samples, where as forsterite is found only in the sample developed from Indian magnesite due to presence of silica as impurities.

© 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Magnesite; Spinel; Reaction-sintering; Dilatometry; Microstructure

1. Introduction

Magnesium aluminate spinel is one of the important refractory material used mainly in steel and cement industries. It is slowly replacing the chrome based spinel, which is also a popular refractory in these industries. However, use of magnesite chrome and Al_2O_3 -chrome is slowly diminishing due to creation of environment hazard of chromium in its hexavalent form [1,2]. Mag-Al spinel possess excellent refractories properties like high refractoriness, moderate thermal expansion, thermal shock resistance and corrosion resistance against steel slags [3,4]. Densification of spinel by single firing process requires a very high temperature (> 1700 °C) as spinel formation from its constituent oxides is accompanied by nearly 7% volume expansion [5,6]. On the other hand the expansion during spinel formation is advantageous in Al_2O_3 -MgO-C (AMC) brick, because at the time of application the expansion due to in-situ spinel formation minimises the gap between bricks joints and stops metal infiltration [7–9]. Different authors carried out research on formation and sintering of spinel by changing the raw material and processing steps. Mansour

et. al. revealed [10] that maximum spinel formation occurred when the calcination temperature of starting material MgCO_3 and $\text{Al}(\text{OH})_3$ were 900 °C and 1100 °C respectively. Gray [11] postulated that hydroxide of constituent oxides improves spinel formation and densification of Mag-Al Spinel. Kostic et. al. found [12] that fine grinding of starting materials increases surface area and structural imperfection, which results in low temperature spinel formation.

Magnesia-rich magnesium aluminate spinel is mainly used in cement rotary kilns due to its compatibility with the products obtained during cement formation. Alper in his MgO - Al_2O_3 binary system study showed that MgO solubility in spinel phase is 39% [13]. Bailey et. al. found that excess MgO in spinel phase restricts grain growth of spinel and thereby facilitates sintering [14]. Cooper et. al. found that 40% magnesia in magnesia-spinel brick improved thermal and corrosion properties [15].

India has large reserve of magnesite which contains detrimental impurities like CaO , SiO_2 , Fe_2O_3 and that limits its high temperature applications. In the present study, natural Indian magnesite, which contains SiO_2 and CaO as detrimental impurities, was used to develop magnesia-rich magnesium aluminate spinel aggregates and compare its properties with the aggregates developed from synthetic calcined magnesia.

*Corresponding author. Tel.: +91332322 3481; fax: +91 332473 0957
E-mail addresses: arup@cgcric.res.in, arupcgcri1@gmail.com (A. Ghosh).

2. Experimental

The raw materials used in this investigation were natural Indian magnesite of Salem origin of Tamil Nadu (India), caustic calcined magnesia of Nedmag Industries, The Netherlands and calcined alumina (SRM 30) of Hindalco Industries, India. Salem magnesite was crushed and ground to – 60 mesh BS sieve. Two batches were prepared one with Salem magnesite (SS) and the other with the Nedmag magnesia (NS) keeping same calcined alumina. The final ratio of MgO: Al₂O₃ was maintained as 2:1 i.e., Al₂O₃ 56 wt% and MgO 44 wt% respectively in both the batches. The batch containing Salem magnesite was calcined at 850 °C for 2 h in order to convert magnesite to magnesium oxide. These batches were individually attrition milled using zirconia pot with partially stabilized zirconia (PSZ) grinding media in ethanol medium. Slurry thus obtained was kept overnight for natural drying followed by oven drying at 100 ± 5 °C for 24 h. The dried materials were crushed to break the agglomerate and passed through 100 mesh sieve to get the desired fine powder. The powder was uniformly mixed with 5% polyvinyl alcohol (PVA) solution as green binder and uni-axially pressed into bars (size 60 mm × 6 mm × 6 mm) and pellets (dia 20 mm × 5 mm) under the specific pressure of 100 MPa. The green bars and pellets were dried in an oven at 110 ± 5 °C after 24 h natural drying. Dilatation behaviour of the samples was investigated in a vertical thermo mechanical analyser (TMA) in air atmosphere. The dried samples were subsequently sintered in the temperature range of 1500–1600 °C. Firing was done in a programmable electric furnace in oxidizing atmosphere and the heating rate was maintained at 5 °C/min from room temperature to 1000 °C and from 1000 °C to peak temperature at a rate of 3 °C/min with 2 h holding time at peak temperature followed by natural cooling to room temperature. The sintered samples were characterized in terms of bulk density (BD), apparent porosity (AP), hot modulus of rupture (HMOR), microstructure and phase assemblage. BD and AP were measured by standard liquid displacement method using Archimedes principle in kerosene medium. The crystalline phases of sintered samples were identified by X-ray diffraction technique. The X-ray diffraction patterns of the finely powdered samples were obtained by Philips X-ray diffractometer (Model PW 1730) using nickel filtered Cu-K_α radiation with a scanning rate 2° (2θ) per minute and diffraction patterns were recorded over a Bragg's angle (2θ) range of 15° to 80°. Microstructural analysis of the polished surface of the samples was performed by scanning electron microscopy after thermal etching (Supra 35VP Zeiss). Grain size was measured by line intercept method using SEM photomicrographs of the samples. Hot modulus of rupture of the sintered bar samples was tested by three point bending method at 1300 °C.

3. Results and discussion

The chemical analysis of the raw materials (Table 1) shows that the natural magnesite of Salem region contains considerable amount of SiO₂ and CaO as impurities which reduces the

MgO content in the magnesite to 85% (loss free basis). Whereas, the caustic calcined magnesia is pure in nature (MgO-98.6%) with negligible quantity of minor impurities. Calcined alumina is highly pure with Al₂O₃ content more than 99%. X-ray analysis reveals that magnesite (MgCO₃) is the major phase in natural magnesite along with small amount of quartz phase. The crystalline phases present in caustic calcined magnesia and calcined alumina are periclase and corundum respectively.

Dilatometric curves of the green compacts of magnesia rich spinel samples (NS & SS) are shown in Fig. 1. The monotonous expansion up to around 1100 °C is a typical thermal phenomenon and not connected to spinelisation reaction [16–18]. The sharp increase in expansion beyond 1100 °C is primarily due to spinel formation, as spinelisation is accompanied by 5–7% volume expansion [16]. Simultaneously, particle rearrangement and densification process are also taking place which have opposite effect to expansion. It has been observed that in case of SS, the expansion is much less as compared to NS sample. It indicates that in SS batch, densification starts early (at a lower temperature) which compensate the expansion due to spinel formation. In both the cases, with the increase in temperature, expansion reaches maxima and after that it starts decreasing. At this point the rate

Table 1
Physicochemical properties of the starting raw materials.

Properties	Raw Magnesite	Caustic Magnesia	Calcined Alumina
Chemical Constituents (wt%)			
SiO ₂	11.54	0.06	–
Al ₂ O ₃	0.26	0.23	99.3
Fe ₂ O ₃	0.6	0.05	–
CaO	2.6	0.8	–
MgO	85	98.6	–
Na ₂ O	–	–	0.3
L.O.I	43.67	7.7	–
Crystalline phase	Magnesite Quartz	Periclase	Corundum

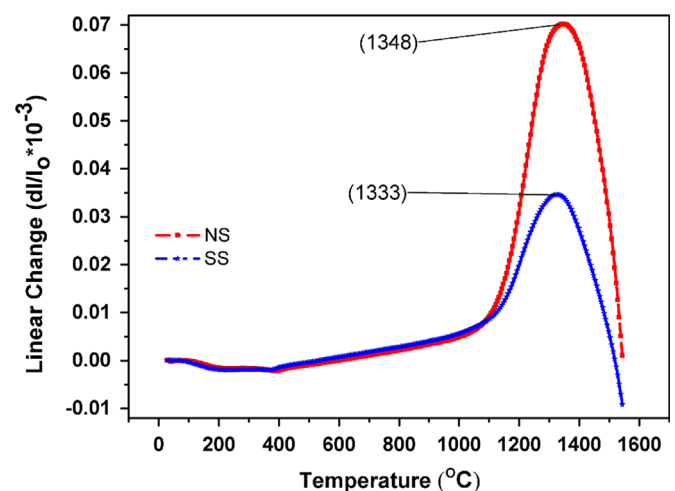


Fig. 1. Dilatometric behaviour (TMA) of green compacts of SS (solid line) and NS (dotted line).

Download English Version:

<https://daneshyari.com/en/article/10624391>

Download Persian Version:

<https://daneshyari.com/article/10624391>

[Daneshyari.com](https://daneshyari.com)