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Influence of nano boehmite on solid state reaction of alumina and magnesia

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ABSTRACT

Effect of nano boehmite on formation of alumina–magnesia spinel via solid state reaction is reported. Various amounts of nano boehmite were added to Al_2O_3–MgO mixtures and the mixtures were heated at different temperatures ranging from 800 to1500 °C for 2 h. Phase structure and chemical composition of the samples were evaluated by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), and differential thermal analysis (DTA) techniques. Scanning electron microscopy (SEM) was also employed to study microstructure of the fabricated samples. It was revealed that the formation temperature of $MgAl_2O_4$ spinel decreased significantly in the presence of nano boehmite. The initial spinel layer formed on magnesia particles was believed to play a mineralizing effect, and, therefore, accelerate the solid state reaction between magnesia and alumina. Nano boehmite also discouraged formation of hybonite (CA6) phase. The results are explained with emphasis on the importance of low temperature spinel formation in refractory materials.

1. Introduction

Spinel-type oxides are compounds with the general chemical formula AB_2O_4. Generally, the A cation is tetrahedrally, and the B ion octahedrally coordinated, although inverse spinel structures are possible as well, in which B ions, partially or fully, occupy tetrahedral positions and A ions reside in the octahedral sites. Many elements can be accommodated in spinel or spinel-like structures which allows for a wide array of possible spinel formulations, and a correspondingly large flexibility for tailoring these oxides for specific applications. As such, spinels find use in many applications due to their optical, magnetic and (electro) chemical properties, examples of which are cathodes, sensors, phosphors in solid state lasers as well as catalysts, and [1–9] refractory [10–15]. The most common refractory spinel structure is $MgAl_2O_4$ in which 8 of 64 tetrahedral sites are occupied by Mg^{2+} and 16 of 32 octahedral sites are occupied by Al^{3+} [9]. Magnesium aluminate spinel ($MgAl_2O_4$) denoted as MA is an ecologically benign refractory material. It offers a desirable and unique combination of mechanical, chemical and thermal properties both at ambient and elevated temperatures. It possesses high-melting point, high chemical inertness against both acidic and basic slags, low expansion values at elevated temperatures [11,12], The major application areas of spinel refractories are transition and burning zones of cement rotary kilns (magnesia–spinel refractories), side walls and bottom of steel teeming ladles (alumina spinel castable), and checker work of glass tank furnaces regenerators [13]. Therefore, the preparation of high purity magnesium aluminate spinel using a low cost-effective route is important.

Over the last few decades, numerous techniques have been used to prepare high purity magnesium aluminate spinel powder including solid-state synthesis hydrothermal synthesis [14], co-precipitation [15–17], microemulsion technique [18], microwave-assisted combustion processing [19], plasma spray decomposition [20,21], sol–gel of double or semi-alkoxides [22–24], the citrate–nitrate route [25,26], organic gel-assisted citrate process [27], aerosol method [28], freeze drying [29], decomposition of organometallic compounds [30–33], mechaniochemical synthesis [34,35], mechanical activation [1] and others [36–38]. Among them solid-state synthesis is the most common rout to produce commercial MA spinel. In this technique, the reaction in the solid phase takes place between MgO and Al_2O_3 raw materials over a temperature range of 1200–1400 °C for commercial practice [39]. Although the conventional solid-state rout is the simplest method to fabricate this spinel, it is suffering from intensive energy and time consumption. Therefore, the scientists have been investigating several types of materials as mineralizer to encourage spinel formation in this process [40]. As an illustration, salt vapors were reported [5]

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Table 1
Physical and chemical properties of starting materials.

	Alumina	Magnesia	Nano boehmite
Al_2O_3	99.6	–	73
Na_2O	0.1	–	0.002
SiO_2	0.01	0.92	–
MgO	–	97.46	–
CaO	–	0.8	–
L.O.I. (1100 °C)	0.3	0.6	–
d_{50} (μm)	3	<150	45
Dispersion particle size (nm)	–	–	25
Phase content	Corundum (C)	Periclase (P)	Boehmite (B)

as useful additives for formation of spinel. Fluoride ions (from AlF_3 or CaF2) were also found [41] to enhance the spinel formation by replacing oxygen in the structure. Formation of up to 98% spinel in a stoichiometeric composition at 1300 °C in the presence of 1 wt% cryolite (Na_3AlF_6) was reported [42]. These additives, however, all have some shortcomings including lowering the melting point and deteriorating some physical properties.

This study sheds light on the effect of addition of nano boehmite on formation temperature of $MgAl_2O_4$ spinel. The influence of nano boehmite content and firing temperature on phase structure was also investigated via quantitative X-ray diffraction technique.

2. Experimental

Magnesia, alumina, and nano boehmite powders, whose physical and chemical properties are presented in Table 1, were used as starting materials. Alumina and magnesia powders with stoichiometric ratio (1:1 molar fraction) were ball milled for 1 h and, then, added to the nano boehmite suspension. Details of the samples preparation route can be found in our previous work [43]. Afterward, the mixtures were uniaxially pressed under the pressure of 30 MPa to make pellets with dimensions of d = 25 and h = 7 mm. Then, the samples were fired at different temperatures ranging from 700 to 1500 °C with +100 °C intervals. Heating rate and soaking time were same for all samples and considered as 5 k/min and of 2 h, respectively.

Differential scanning calorimetry analyzer (Netzch) was employed to study phase transformations in the samples. Moreover, phase structure of the samples was evaluated by X-ray diffraction technique (Philips, Xpert). Normalized relative intensity ratio (RIR) method was also utilized in order to quantitative phase study of powdered pellets [44]. Microstructure of the samples was also investigated by scanning electron microscopy (Tescan, Vega II XL) equipped with electron diffraction energy dispersive X-ray spectroscopy.

3. Results and discussion

Fig. 1 illustrates the DTA results of the fabricated samples. Only one endothermic broad peak around 1190 °C is observed in the DTA curve (a) which corresponds to the sample without nano boehmite. The peak can be attributed to solid state reaction between Al_2O_3 and MgO to form $MgAl_2O_4$ spinel. The significant broadness of the peak reveals diffusion nature of this reaction. In contrast, the DTA curve (b), which is assigned to 7 wt%-boehmite sample, depicts two endothermic peaks at temperatures of 800 and 1150 °C. The peak located at 800 °C could be attributed to a primary spinel formation via the reaction between γ-alumina from nano boehmite decomposition and MgO particles (compare this curve with DSC curve of nano boehmite (Fig. 1b)) [45,46]. According to Fig. 2, it can be concluded that boehmite mostly decomposed to γ-Al_2O_3 and a few amount of δ-Al_2O_3 which are active enough to react with MgO at low temperatures [47]. The peak at 1150 °C is related to the conventional solid state reaction between alumina and magnesia, as elucidated earlier.

XRD patterns of the samples without nano boehmite, fired at different temperatures, are depicted in Fig. 2. The patterns show that no chemical reaction takes place between alumina and magnesia below 900 °C. However, the XRD characteristic peaks of $MgAl_2O_4$ appear when firing temperature increases to 1000 °C. The higher the firing temperature the more intensive the spinel characteristic

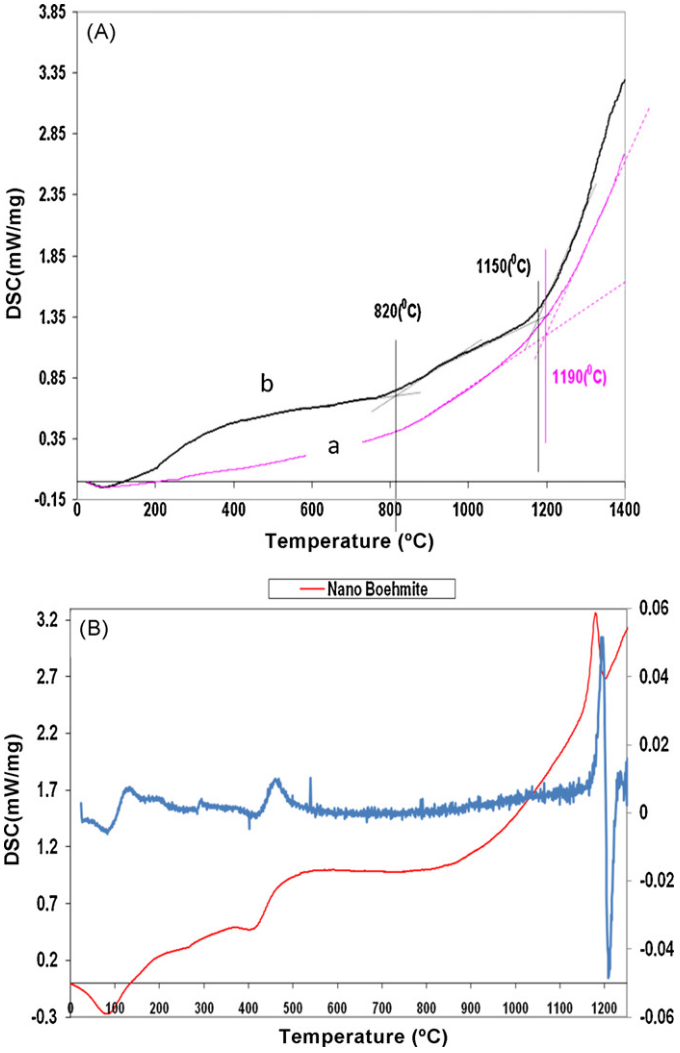

Fig. 1. (A) DSC spectra of the samples containing (a) no nano boehmite and (b) 7 wt% nano boehmite. (B) DSC spectra of nano boehmite.

peaks are. In addition, the CA_6 phase forms in the sample fired at 1500 °C. This result is in a good agreement with the results reported by other scientists [48,49].

Fig. 3 represents XRD spectra of the samples with 7 wt% nano boehmite fired at various temperatures. It is seen that the inten-

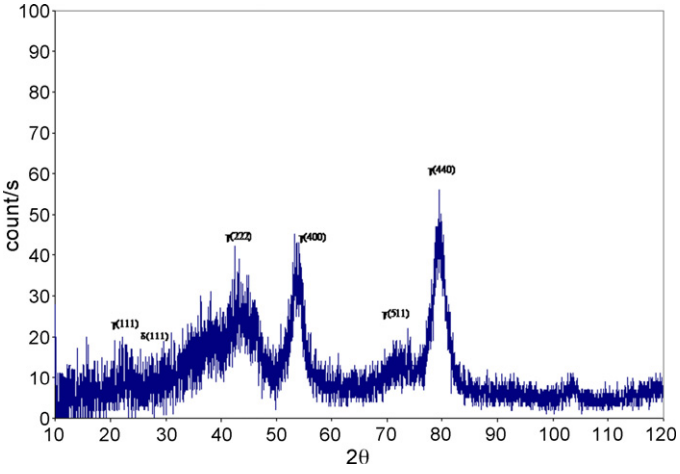

Fig. 2. XRD pattern of nano boehmite fired at 800 °C for 2 h.

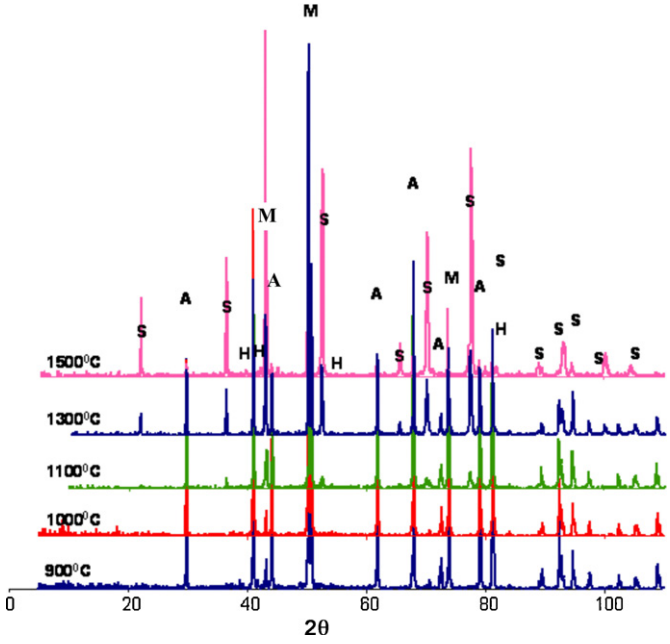

Fig. 3. XRD patterns of the samples containing no boehmite fired at different temperatures.

sity of spinel peaks increases with firing temperatures. The main difference between these XRD patterns and the previous ones is that the characteristic peaks of $MgAl_2O_4$ spinel appeared at the firing temperature of 800 °C. In order to evaluate the influence of nano boehmite on formation temperature of $MgAl_2O_4$ spinel, phase structure of the samples with different amounts of nano boehmite was studied whose results are exhibited in Fig. 4. It should be mentioned that all of these samples were fired at 1100 °C. It is obvious that the intensity of spinel peaks increases gradually with amount of the nano boehmite; that is, adding more nano boehmite results in formation of more spinel. The results also show that alumina and

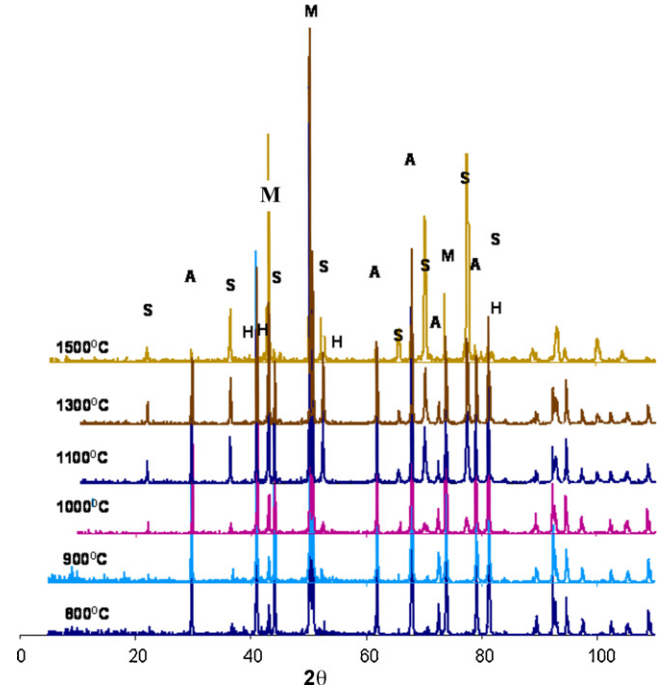

Fig. 4. XRD patterns of the samples containing 7 wt% nano boehmite fired at different temperatures.

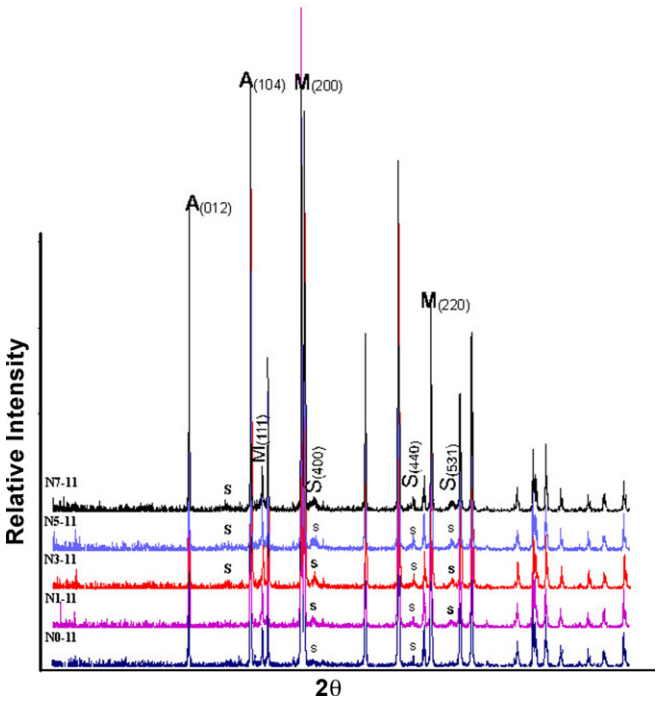

Fig. 5. XRD patterns of the samples containing different amounts of nano boehmite at 1100 °C.

magnesia are the prevailing phases at temperatures below 1400 °C in the samples with and without nano boehmite. However, formation temperature of spinel decreased from 1000 to 800 °C when nano boehmite was added to the samples.

Weight fraction of spinel was calculated using normalized relative intensity ratio (RIR) method [50] results of which are presented in Fig. 5. As is seen, addition of 3 and 7 wt% nano boehmite to the samples, respectively, resulted in formation of about 13 and 20 wt% $MgAl_2O_4$ even at low firing temperatures (900 °C). Clearly, more spinel formed in the samples containing nano boehmite at all temperatures. The reason for such a behavior is that nano boehmite plays a seeding role and encourages formation of more spinel [51,54]. Weight percent of the formed spinel differs significantly in the samples with and without nano boehmite at the firing temperature of 900 °C; furthermore, this difference decreases with increasing the firing temperature. In fact, at lower temperatures nucleation controls the reaction, while at higher temperatures growth is the determining phenomenon [55] (Fig. 6).

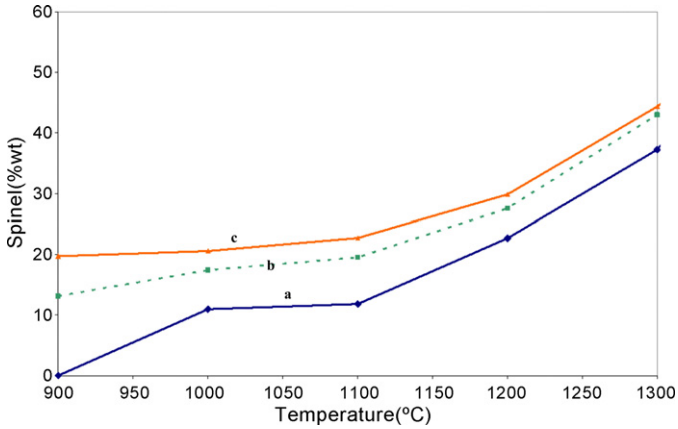

Fig. 6. Quantitative XRD analysis for the samples containing: (a) no nano boehmite, (b) 3 wt% nano boehmite, and (c) 7 wt% nano boehmite.

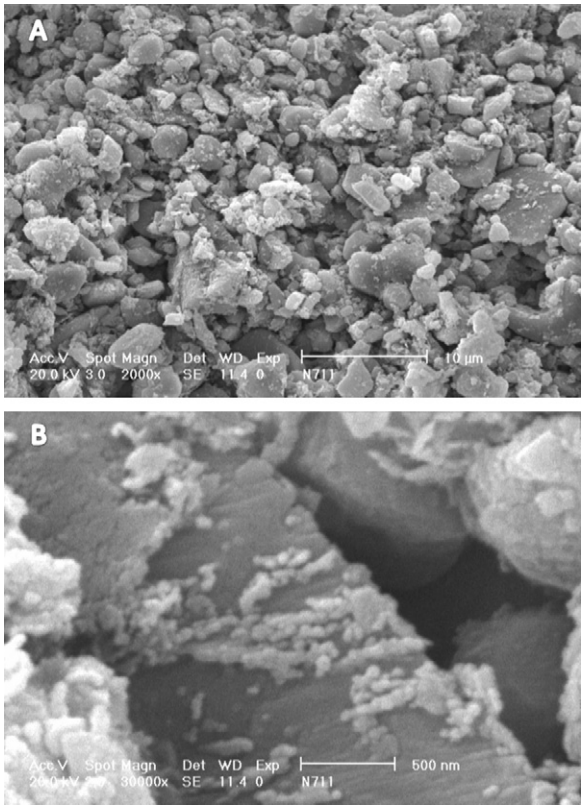

Fig. 7. SEM images of the samples fired at 1500 °C containing: (a) no nano boehmite and (b) 7 wt% nano boehmite.

Table 2
The effect of nano boehmite on the spinel content.

Nano boehmite content (wt%)	Expected value (wt%)	Detected value (wt%)
3	$(3-3\times0.15)/0.72=3.54$	13
7	$(7-7\times0.15)/0.72=8.26$	20

Table 2 shows the detected and expected values of spinel as a function of the firing temperature for different nano boehmite amounts. A significant difference between detected and expected values is observed. This difference is illustrated by the seeding effect of nano spinel particles formed by the reaction of magnesia and nano boehmite at low temperatures. The formed nano spinel particles accelerate the reaction between micro-sized magnesia and alumina.

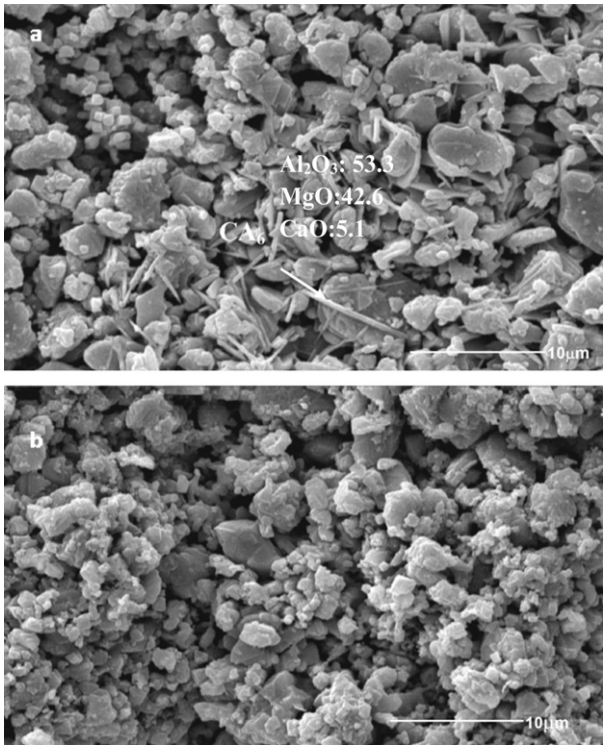

Fig. 9. SEM morphology of the bright coat formed on the surface of magnesia at different magnifications.

Microstructure of the samples containing 7 wt% nano boehmite is shown in Fig. 7. As is seen, fracture surface of the sample was covered by a spinel layer due to nano boehmite addition. Higher magnification image reveals that the layer consisted of nano particles. Our EDX analysis showed that this layer consisted of spinel. Two anomalies are seen in these microstructures. First, the formed spinel layer mostly covered magnesia particles while it should have mostly covered alumina particles based on the Wagner theory, where he explains as a consequence of the higher diffusion rate of Mg^{2+} into Al_2O_3, more spinel forms on alumina particles than magnesia one [56]. Second, it was deduced that formation of this spinel layer over magnesia grains should have retarded spinel formation. In former case, since nano-sized alumina powders were applied on the surface of micron sized magnesia, then the formation of spinel occurs on magnesia consequently. For the later, Watson et al. proposed that diffusion of Al^{3+} to MgO at MgO/spinel interface and Mg^{2+} at Al_2O_3/spinel interface are the main factors affecting and controlling formation of $MgAl_2O_4$ spinel and no con-

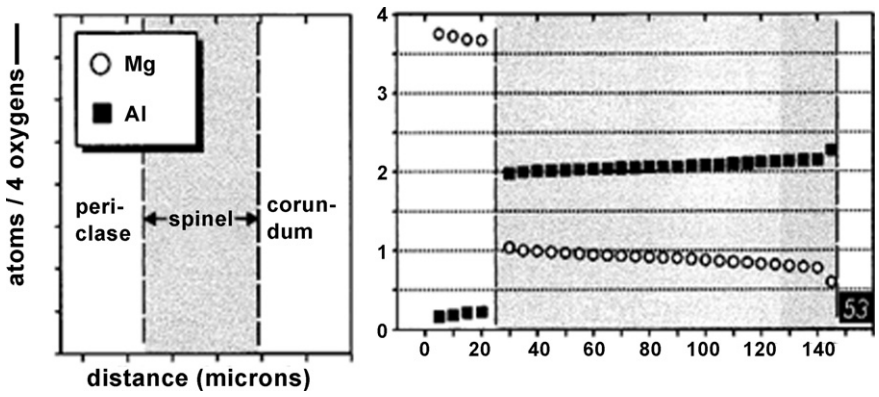

Fig. 8. Distribution of cations within the formed spinel [57].

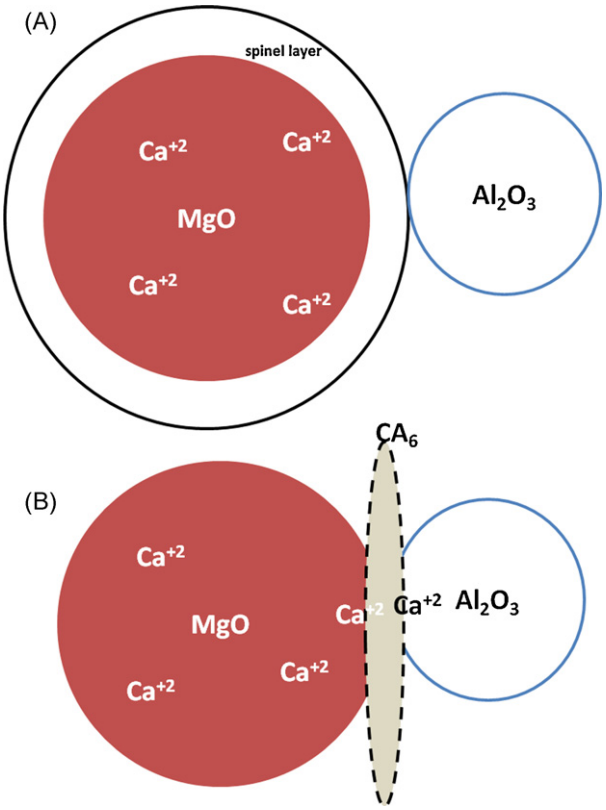

Fig. 10. Schematic illustration of formation mechanism of CA_6 phase in: (a) sample containing nano boehmite and (b) samples without nano boehmite.

centration gradient within formed spinel layer (Fig. 8) was observed based on their EMP studies [57]. Therefore, it is concluded that low temperature primary spinel does not suppress spinel formation.

Microstructure and elemental composition of samples with and without nano boehmite, obtained by SEM/EDS, is compared in Fig. 9. It is seen that in the presence of nano boehmite, formation of hybonite (CA_6) phase retarded. This phase forms due to the reaction between impurities (CaO) of magnesia and alumina [31]. Impurities of magnesia can react with alumina in the absence of nano boehmite. However, a spinel layer forms on the magnesia grains when nano boehmite is added to the sample. This layer inhibits diffusion of Ca^{2+} ions into the unreacted alumina, and, therefore, formation of CA_6 phases is suppressed [58–60]. Fig. 10 schematically illustrates the proposed mechanism.

4. Conclusions

The effect of nano boehmite on solid state reaction between alumina and magnesia to form $MgAl_2O_4$ was investigated, and the following results were obtained:

1. $MgAl_2O_4$ spinel forms at temperature below 800 °C in the presence of nano boehmite.
2. O Nano boehmite causes formation of nano spinel over the surface of magnesia particles which encourages spinel formation at all temperatures.
3. In the presence of nano boehmite, formation of low melting hybonite phase is retarded.

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