

The influence of nano boehmite on spinel formation in the alumina-magnesia system at low temperatures

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The effect of nano boehmite on the formation of spinel at low temperatures ($T < 1000^{\circ}\text{C}$) in the alumina-magnesia system via a solid-state route is investigated. The homogeneity of prepared mixtures was studied carefully by X-ray diffraction, FTIR¹ and SEM/EDX. This clarified that the formation of spinel was encouraged in the presence of nano boehmite. It was also found that the primary spinel formed via a solid-state reaction was in the nano size range and possessed a cubic morphology. The importance of the present study is explained with an emphasis on refractory applications.

Key words: Spinel, Nano Boehmite.

Introduction

Due to the combination of physical, chemical, optical, dielectric and mechanical properties including high melting temperature, high strength at elevated temperatures, relatively high thermal shock resistance beside incredible inertness to chemicals and especially towards neutron irradiation, alumina magnesia spinel (MgAl_2O_4) is one of the most important multi-applicable materials. Spinel² has been applied in industry in, humidity sensors and catalyst supports, as spinel bond in refractories, as a transparent optical ceramic, which is an integral component (e.g. radomes, IR domes, sensor protection, and multi-spectral windows) of many advanced weapon systems. The drawback that limits its application is the difficulty of proper synthesis. Several processes like freeze-drying [1], hydroxide co precipitation, sol-gel, thermal decomposition, flame spray pyrolysis, hydrothermal process [2] and combustion synthesis have been introduced up to now. Although several routes exist for the preparation of magnesium alumina spinel, consideration of affordability and versatility of a route still remain as a major challenge for materials scientists involved in the development of new synthetic routes. By the way, as result of economical and environmental limitations, a solid-state procedure is the most convenient method for alumina magnesia spinel production industrially. Although, a solid-state route is convenient but the high temperatures that are needed to produce a dense spinel besides the high volume expansion that occurs during spinel formation, force scientists to work

on additives in order to reduce these problems. There are two types of additives, a mineralizer and sintering additives, the first group reduces the spinel formation temperature and later improves spinel sinterability. Furthermore, the effects of different additives on the development of spinel have been extensively studied. Salt vapors were reported [3] to be useful additives for the development and formation of spinel. Fluoride ions (from AlF_3 or CaF_2) were found [4] to enhance the spinel formation by replacing oxygen in the structure. Sintering was also found to be improved by using rare earth oxides such as 4 wt.% of Yb_2O_3 and Dy_2O_3 , [5] etc. Cr_2O_3 was reported to improve the thermal shock resistance and slag resistance of the periclase spinel bodies. Researchers found the addition of TiO_2 to spinel causes a continuous improvement in densification due to exsolution of alumina and dissolution of TiO_2 in the spinel. Ghosh et al. [6] obtained 99% densification in magnesium alumina spinel using ZnO as an additive and suggested the formation of anion vacancies in the presence of ZnO results in improved density and mechanical properties. Chen et al. [7] found 98% spinel formation in a stoichiometric spinel composition at 1300°C in the presence of 1 wt.% cryolite (Na_3AlF_6). A study of the addition of Y_2O_3 on spinel ceramics is also available in the literature. In fact, different authors reported increased sinterability of high quality spinel in the presence of 5 wt.% of Y_2O_3 [8]. The seed effect of spinel as an additive was also studied by Pasquier [9]. It is reported that magnesia alumina spinel improves spinel formation and monitors its expansion properties.

In this article, the effect of nano boehmite as an additive on spinel formation is investigated. For that,

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¹Fourier Transformer Infra-Red

²Spinel stands for MgAl_2O_4 for whole the text.

Table 1. Raw Material analysis (Wt %) and characteristics

	Alumina	Magnesia	Nano Boehmite
Al ₂ O ₃	99.6	–	73
Na ₂ O	0.1	–	0.002
SiO ₂	0.01	0.92	–
MgO	–	96.46	–
L.O.I (1100°C) (%)	0.3	0.6	–
d ₅₀ (μm)	3	<150	45
Dispersion particle size (nm)	–	–	25

nano boehmite is added to a stoichiometric composition of magnesia and alumina to form in situ nano spinel so that its role as a mineralizer on magnesium alumina spinel could be understood.

Experimental Procedure

Table 1 gives the analysis and characteristics of the raw materials used in the present study. The particle size of alumina and magnesia were chosen based on the ones used in the refractory industry. The alumina, magnesia and nano boehmite (NB) were obtained from FIBRONA, NEDMAG, and SASOL companies respectively. XRD³ and DTA⁴ patterns of nano boehmite are present in Fig. 1.

The XRD pattern (Fig. 1a) shows a pure boehmite phase and our measurements on particle size based on

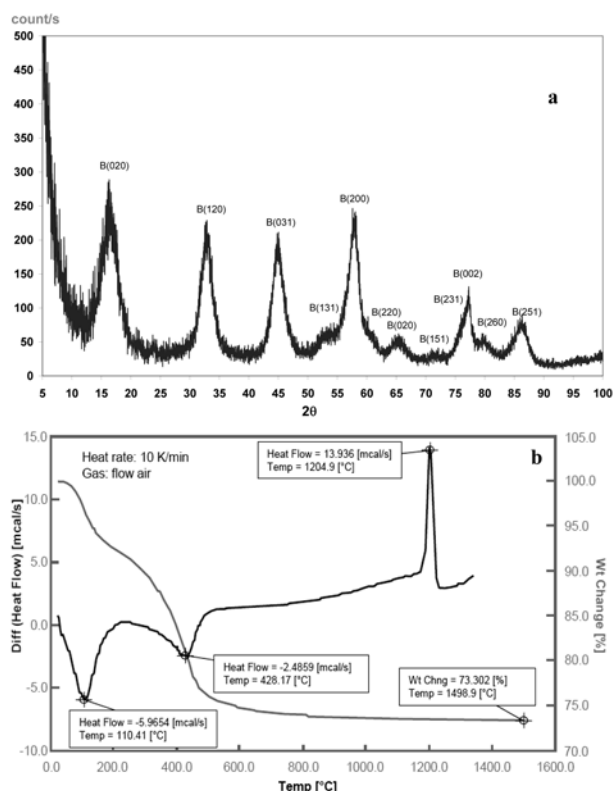


Fig. 1. a) XRD pattern of nano boehmite. b) DTA/TG of as received nano boehmite.

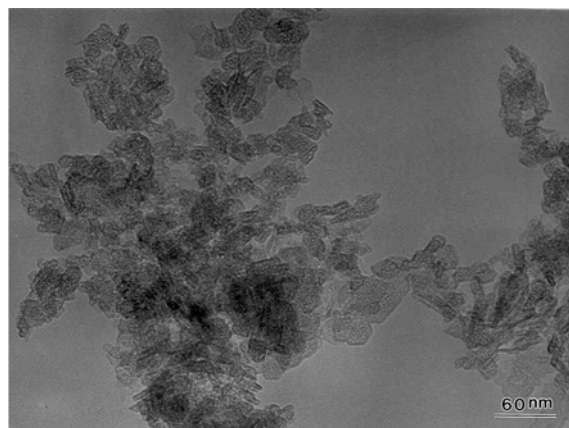


Fig. 2. TEM⁸-image of Disperal P2, needle-shaped particles.

the Scherer equation [10] gave us an average crystallite size of <10 nm which is in reasonable agreement with the 25 nm particle size claimed by the manufacturer. Thermal analysis of nano boehmite (Fig. 1b) shows two endothermic and exothermic peaks, the first two peaks at 110°C and 428°C one attributed to moisture release and structural water decomposition. The last one at 1204°C is related to alpha alumina formation. In fact, alumina first forms at 428°C in the form of gamma alumina goes through a series of allotropic phase transformations until 1204°C where it completely transforms to alpha alumina.

TEM investigation was used to display the morphology of the dispersed nano boehmite (Fig. 2). Two types of mixtures consisting of alumina-magnesia-NB and magnesia-NB were then prepared to establish the effect of NB as a mineralizer preciously studied.

In order to prepare samples, alumina and magnesia powders were dry ball milled in a polymeric vessel where 50 grams of alumina balls were used for 100 grams of batch. Simultaneously, NB powders were dispersed in double distilled water by magnetic stirring for 30 minutes in a glass beaker.

Alumina magnesia mixture (MA) was then gradually added to the stirring dispersion followed by drying up at 80°C for 24 hr. The pulverized powder was later passed through 100-mesh sieve to obtain homogeneous powder. Pellets of $\phi 25 \times 4$ mm were prepared in a cylindrical die under 30 MPa pressure. The samples were fired at desired temperatures according to the thermal regime that shown in Fig. 3. Phase analysis and microstructural evaluation were then performed on fired samples using XRD and SEM⁵.

³X-Ray diffraction

⁴Differential Thermal Analysis

⁵Scanning Electron Microscopy

⁸Transmission Electron Microscopy

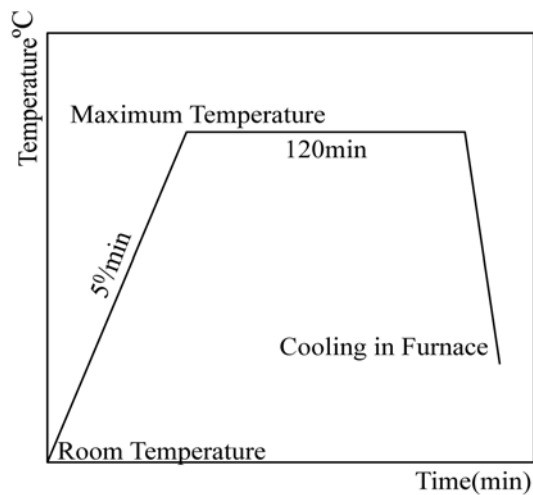


Fig. 3. Heat treatment curve.

Results and Discussion

Homogeneity evaluations

Due to the importance of a homogeneous distribution of additives in the mixture, particularly, when additives are nano size, the homogeneity of the system was evaluated by different methods.

The XRD peak intensity is a criterion of phase presence and comparison of peak heights of the samples taken from different parts of a particular batch could give an indication of homogeneity in the mixture (Fig. 4). For this, 0.5 gram of each sample was prepared as standard for XRD examinations. It should be noted that operator was the same during these experi-

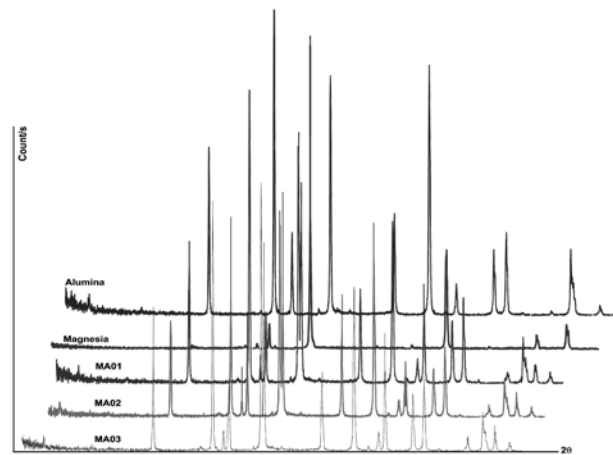


Fig. 4. XRD patterns of MA mixtures.

ments. The ratio of the relative intensity of alumina (I_A) and magnesia (I_M) at specified peaks is calculated and percent of deviation of them is regarded as a homogeneity index (H):

$$H = I_A/I_M$$

In addition as mentioned before, the percent of deviation of height of specified peaks in counts was calculated to show the homogeneity of the alumina and magnesia distribution (Table 2) [10].

Furthermore, to insure that calculations were close to the real state, MAP was performed on MA. Figure 5 illustrates that the distribution of magnesia in alumina is uniform.

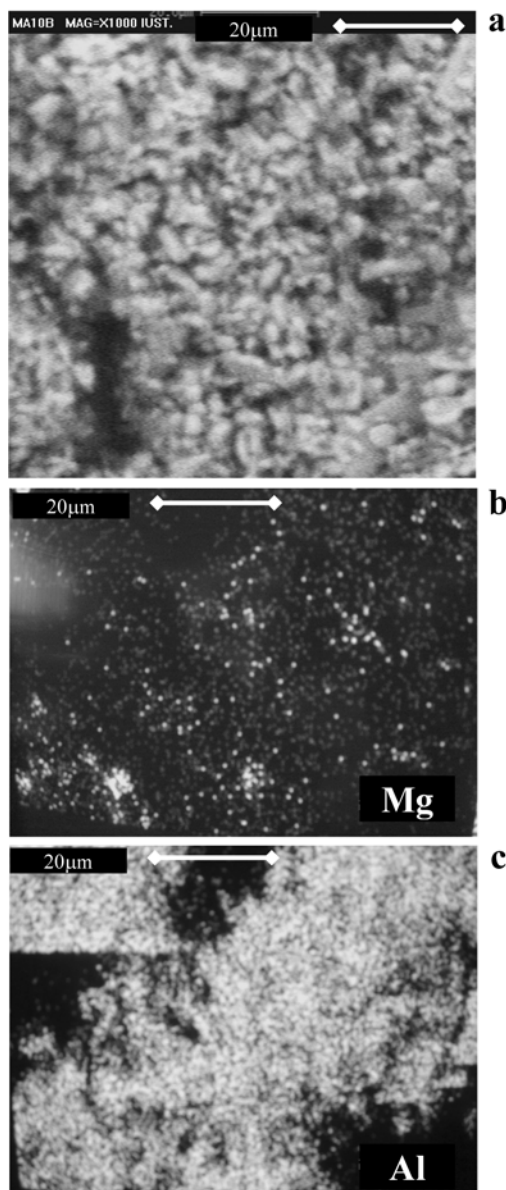
As with MA mixtures, NB added mixtures were also

Table 2. Homogeneity calculations of MA mixtures

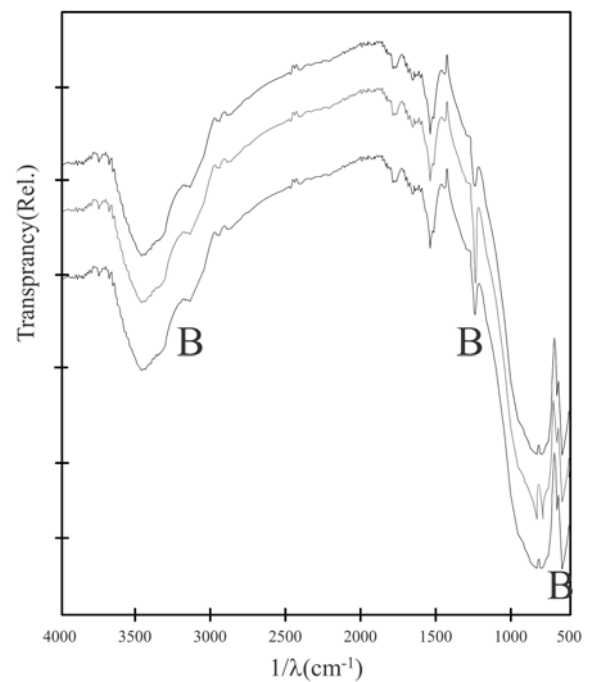
	Peak NO.	2Teta	I/I0	H:A3/M1	H:A1/M1	H:A2/M1
MA01	A1	29.91523	31.34	0.8927	0.3134	0.7741
	A2	41.18965	77.41			
	A3	68.02771	89.27			
	M1	50.394	100			
	M2	73.89962	55.24			
	M3	89.56148	7.7			
MA02	A1	29.89487	30.83	0.9238	0.3083	0.7739
	A2	41.22882	77.39			
	A3	68.04419	92.38			
	M1	50.36884	100			
	M2	73.97613	60.85			
	M3	89.61816	8.62			
MA03	A1	29.94878	35.85	1.01461	0.3637378	0.8731737
	A2	41.22652	86.06			
	A3	68.08678	100			
	M1	50.38457	98.56			
	M2	73.95154	50.61			
	M3	89.64377	5.89			
%Deviation				6.334545	3.0641092	5.72580505

Table 3. Homogeneity Calculations for MAB mixtures

F:P2/P3	F:P3/P1	F:P2/P1	P3 3300	P2 3100	P1 1072	
1.04979684	0.91631268	1.04979684	39.691	45.473	43.316	MA10B1
1.03155174	0.93038156	1.03155174	51.839	57.476	55.718	MA10B2
1.06132725	0.86036534	1.06132725	38.103	47.003	44.287	MA10B3
1.04015684	0.91385546	1.04015684	54.071	61.544	59.168	MA10B4
1.07804574	0.87259061	1.07804574	37.846	46.757	43.372	MA10B5
1.0349167	0.97960352	1.0349167	71.85	75.907	73.346	MA10B6
1.00744603	0.92445293	1.00744603	62.946	68.597	68.09	MA10B7
1.0323968	1.00781738	1.0323968	82.251	84.257	81.613	MA10B8
2.26500286	3.93238633	2.26500286	% Deviation			

**Fig. 5.** Microstructure (a), Mg distribution (b), Al distribution (c) X-ray mapping.

tested for homogeneity aspects, by FTIR. This technique was utilized instead of XRD due to the nature of

**Fig. 6.** Typical FTIR patterns of different parts of mixture contain alumina magnesia and 7 percent nano boehmite.

nano boehmite, which consists of hydroxyl groups and significant difference between particle size and quantity of NB and other ingredients (Fig. 6) [11]. The same sample preparation and calculation were also performed and homogeneity factor (F)⁶ is defined alike (Table 3). Since F is less than 4 percent, it is claimed that the amount of NB in different parts of a batch is the same and in other words, NB completely disperses in MA mixtures.

Phase evolution

To evaluate the nano boehmite effect on spinel formation by a solid-state procedure, a variety of samples which had differences in NB content, were fired at 700°C, 800°C, 900°C and 1000°C. Fired samples then characterized by XRD and SEM/EDX. In Fig. 7, XRD

⁶ $F = I_{B1}/I_{B2}$; for instance, I_{B1} : intensity of 1071 cm^{-1}

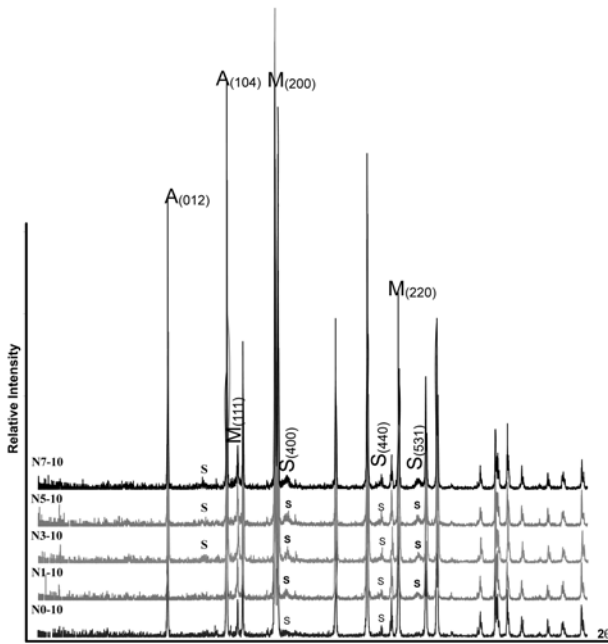


Fig. 7. XRD patterns of nano boehmite added samples fired at 1000°C. A: Alumina, M: Magnesia, S: Spinel.

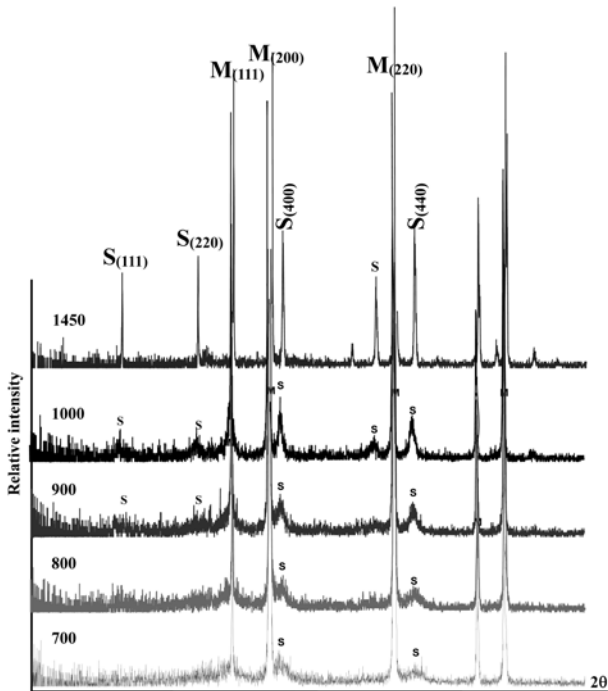


Fig. 8. XRD patterns of magnesia and nano boehmite samples fired at 700 to 1450°C. M: Magnesia, S: Spinel.

patterns of 0 to 7 weight percent NB added samples, fired at 1000°C, are plotted. It is clear that at this temperature, the spinel content considerably increases by increasing the amount of nano boehmite. In addition, since characteristic peaks of spinel are wide, according to Scherer equation the formed spinel is nano crystalline and its crystallite size is below 10 nm. The most important point in Fig. 7 is the clearness of the spinel peak, which has been misunderstood as from

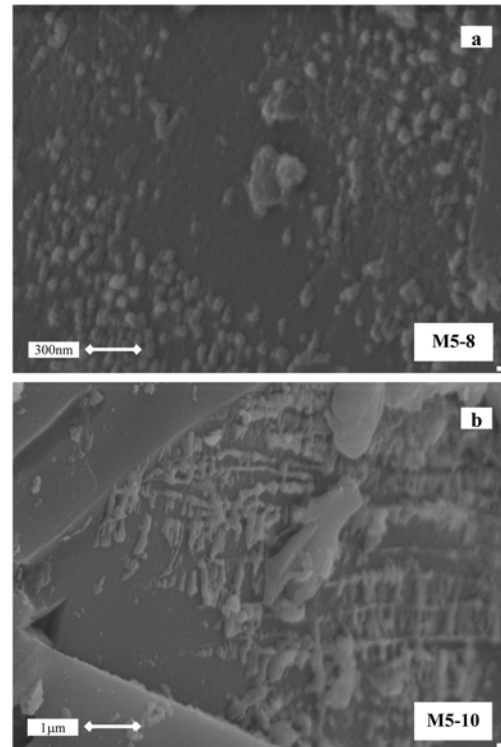


Fig. 9. (A) SEM image of Magnesia 5 wt% nano boehmite fired at 800°C (a), at 1000°C (b).

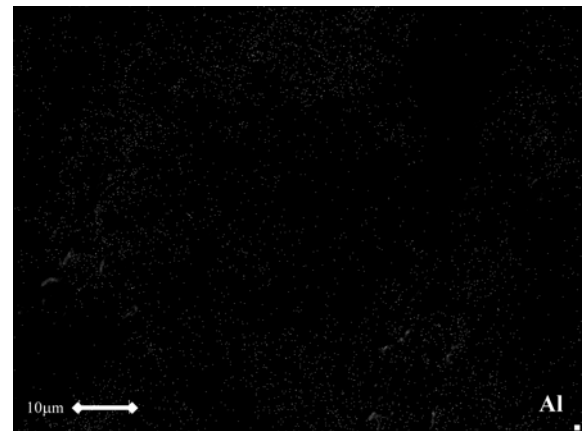


Fig. 10. Aluminum X-ray mapping in magnesia 5 wt% nano boehmite sample.

allotropic phases of alumina. To establish the samples that contain just magnesia and nano boehmite were prepared according to the previous sample preparation procedure and then were investigated.

Figure 8 describes the XRD patterns of fired magnesia and nano boehmite. It illustrates that spinel formation started at 700°C and continued with increasing temperatures.

Comparison between the patterns of Fig. 7 and the ones in Fig. 8 (magnesia-nano boehmite samples) establishes that peaks in the previous samples were correctly assigned as spinel peaks. In addition, the fact that the formed spinel is nano crystallite is validated by applying Scherer equation on the spinel peaks of Fig. 8

patterns. Figure 9-a illustrates how homogeneous cubes of synthesized nano spinel are distributed in magnesia grains which are supposed to encourage spinel formation through a seed effect mechanism. This Figure also implies that nano boehmite had had been previously mixed homogeneously. According to theoretical aspects, such a microstructure can control PLC⁷ in spinel containing refractories. The morphology of the bright phase in M5-10 is individual. In fact, according to EDS, this phase is spinel but it is needle like (Fig. 9-b). In this case it is clear that cubic grains of in situ formed spinel are going to connect to each other and that this behavior is similar to necking in sintering procedure. Because of smaller particle size of spinel nuclei-undetectable by conventional SEM, MAP was carried on for M5-7 sample. As can be seen in Fig. 10, Al is homogeneously distributed in the matrix. Considering this fact that in type 2 mixtures the only source of Al is NB, on the other hand the presence of spinel peaks in the XRD patterns of these samples (Fig. 8), proved that the spinel formed homogeneously at 700°C via a solid-state procedure.

Conclusions

In this article, the effects of nano boehmite on spinel formation investigated. It is deduced that:

Little amount of nano boehmite could be well distributed in a matrix of micro size alumina and magnesia. XRD and FTIR proved to be useful tools to study the homogeneity of such mixtures.

Nano boehmite presence enhanced the formation of MgAl_2O_4 at significant lower temperatures. The nano size in situ spinel could have the seed effect in prompting the alumina and magnesia reaction.

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⁷Permanent Linear Change