Effect of agglomeration during coprecipitation: Delayed spinellization of magnesium aluminate hydrate

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Abstract. Precipitation of magnesium aluminate hydrate with faster addition of ammonia at desired pH causes agglomeration. Agglomerated powder, without any further treatment, on calcination forms intermediate compounds at low temperatures ($\leq 900°C$). The intermediate compounds on further heat treatment ($\geq 1000°C$) decompose into MgO, $MgAl_2O_4$ and α-Al_2O_3. Effect of agglomeration and absorption of foreign ions such as Cl^-, SO_4^{2-}, and NH_4^+ in complex compounds probably cause loss of Al^{3+} and Mg^{2+} ions during heat treatment, and stoichiometry changes. Powders prepared by continuous method with better control of process parameters than batch process yields better spinellization.

Keywords. Agglomeration; stoichiometry; spinellization; solid solution.

1. Introduction

$MgAl_2O_4$ (spinel) has emerged as a potential ceramic material because of its versatile functional properties. Its unit cell is cubic and has a large number of tetrahedral and octahedral sites. Due to its chemical inertness to both acidic and basic slags, it can be used as refractory material in critical applications. Symmetric cubic crystal structure and extraordinary fracture strength (~ 500 MPa) helps polycrystalline Mg–Al spinel ($MgAl_2O_4$) bodies to be used in optical engineering applications such as optical window materials, etc. Spinellization reaction is accompanied by volume expansion (Bailey and Russell 1968), and high pure dense spinel bodies of stoichiometric composition is not easy to fabricate from mixture of Al_2O_3 and MgO powders through solid state sintering route (Bakker and Lindsay 1967). Fabrication process usually consists of a two-stage firing process: spinellization of the mixed powders at $\sim 1600°C$, followed by milling, body making and refiring even at higher temperatures.

Different wet chemical routes have been developed in the recent past to prepare phase pure Mg–Al spinel at relatively low temperatures. Among different techniques such as coprecipitation (Mukherjee and Samaddar 1966; Bratton 1968; Katanic-Popovic et al 1991; Li et al 2001), sol–gel synthesis of metal alkoxides or inorganic salts

(Lepkova et al 1991; Ye et al 2005), combustion synthesis (Behera et al 2004), spray drying (Delau 1970), spray pyrolysis (Suyama and Kato 1982) and flame spray pyrolysis (Bickmore et al 1996) etc, coprecipitation has advantages over other techniques in terms of cost effectiveness, both chemical and phase purity and obviously bulk production. Many investigators prepared Mg–Al spinels by coprecipitation and used different combinations of chemically pure inorganic salts of magnesium and aluminium such as chlorides, nitrates, sulphates, etc. Precipitants such as ammonia, oxalic acid, ammonium carbonate or bicarbonate, etc were used. In most cases, the precipitate was washed, filtered, dried and then calcined to prepare stoichiometric Mg–Al spinel. Some workers (Singh and Sinha 1997; Ye et al 2005) did not consider washing and filtration of the precipitate in order to avoid cation loss (Mg^{2+} or Al^{3+}), and directly dried and calcined the precipitate to achieve stoichiometric composition. Mukherjee and Samaddar (1966) were the first to prepare Mg–Al spinel precursor powder by coprecipitation technique. However, further improvement of the technique in terms of both continuous pilot plant level and batch processes (Samaddar et al 1979) needs further investigation for its product characterization. Previous work (Mukherjee 1968; Bhattacharya and Samaddar 1978) regarding characterization of Mg–Al spinel prepared in laboratory level batch size of 100 g (110°C dried) indicates some abnormality in its phase evaluation during calcination. This observation prompted us to study

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the material's behaviour during calcination, which includes some process manipulation to investigate the changes in phase composition and also $MgO : Al_2O_3$ stoichiometry.

In the present work, coprecipitation techniques (continuous and batch) have been used to prepare magnesium aluminate hydrate (MAH) precursor gel. Products of both the processes were characterized by chemical analysis, particle size distribution, DTA and XRD studies. Quantification of the phases present in calcined powders of both the processes has been done by Rietveld analysis. Some of the results reported earlier have been reviewed for comparison with the present work.

2. Experimental

AR grade magnesium chloride and aluminium sulphate were used to prepare a mixed salt solution having $Mg^{2+} : Al^{3+}$ ionic ratio 1 : 2. Liquor ammonia (AR grade) was used as precipitant for coprecipitation of Mg^{2+} and Al^{3+} as hydrates. Precursor powder prepared by continuous technique was designated as type A, and that of batch process as type B. Temperature during precipitation in both the processes was kept the same.

In the continuous technique (Samaddar *et al* 1979), pH was controlled by an automatic pH control system consisting of motorized ball valve, needle valve, spray gun and flow cell. The gel was precipitated at pH $9 \cdot 2 \pm 0 \cdot 05$, filtered, dried at 110°C until constant weight, and then the hard dried powder lumps were agated. In the batch process, a reactor of 100 litres capacity was designed and bulk precipitation was carried out in the pH range 9·0–9·5 by addition of suitable amount of liquor ammonia. Here the precipitation was rapid and vigorous stirring was continued for 10–15 min. The precipitated gel was filtered and the wet cake was stored in sealed acid–alkali resistant polythene containers. The wet cake was dried at 110°C until constant weight, and then the hard dried lumps were agated. Due to the hydroscopic nature of the dried mass, fineness of dried powders could not be increased beyond a certain limit in both the processes.

Conventional wet chemical method was used to estimate MgO and Al_2O_3 contents in the dried powder. To measure the solid content, LOI was carried out at 1200°C, 2 h. Particle size distribution was estimated (ZetaSizer Nano-S, Model-Zen1600, Malvern, USA) by laser beam technique using sodium hexametaphosphate as dispersing agent to evaluate the extent of agglomeration.

2.1 *Thermal treatment of MAH*

To investigate the thermochemical changes of the dried powders (types A and B) during heat treatment, DTA was conducted up to 1200°C at a heating rate of 10°C/min. Agated powders of both the processes were calcined at 600°, 900°, 1000°, 1200° and 1300°C with 2 h soaking for XRD analysis. Again, to review the effect of agglomeration on extent of spinel formation during calcination, 110°C dried hard lumps of the types A and B were calcined at 1400°C for 2 h. Furthermore, to review whether the precursor hydrates (types A and B) can retain their initial $Mg^{2+} : Al^{3+}$ stoichiometry during spray pyrolysis, these were flash calcined at 900°C for 2 h. Then the flash calcined powders were further heated at 1300°C for 2 h. For XRD studies, all the powders of different temperatures were agated (–200 B S sieve).

2.2 *XRD analysis*

Phase analysis of the calcined powders (types A and B) at each of the temperatures was investigated by XRD (PW 3050/60 Goniometer, PANalytical, The Netherlands). Depending upon the availability, both CuK_α and CoK_α radiations were used. Although due to this, change in '2θ' value would occur for the peaks, XRD curves of only same type of radiation have been incorporated in any individual figure to maintain parity.

3. Results and discussion

Chemical analysis of the 110°C dried samples (table 1) indicates that for both the methods, processing parameters have been closely controlled to precipitate Mg^{2+} and Al^{3+} in the ionic ratio, 1 : 2. Chemical composition of MAH powder suggests that it must yield stoichiometric spinel if there is no loss of cations (Mg^{2+} or Al^{3+}) during calcination. Abnormal LOI values for both the types A and B suggest that MAH powder contained some loosely

Table 1. Chemical analysis of MAH precursors (types A and B).

| Sample identity | Wt% | | LOI (1200°C, 2 h) | Molar ratio ($Al_2O_3 : MgO$) |
	Al_2O_3	MgO		
Type A	22·67	8·66	68·42	1·035 : 1
Type B	21·93	8·60	69·32	1·008 : 1

Table 2. Particle size distribution of MAH precursors (types A and B).

| Particle size (dia in nm) | Mean volume (%) | |
	Type A	Type B
531·2	–	–
615·1	15·0	–
712·4	40·0	–
825·0	35·0	–
955·4	10·0	–
1484·0	–	–
1718·0	–	51·7
1990·0	–	48·3

bonded water molecules beyond OH⁻ group associated with it. Since the precipitation process is rapid and the parent solution contains NH_4^+, Cl^- and SO_4^{2-} ions, it is expected that the precipitated gel is considerably agglomerated and may absorb some of these foreign ions to form intermediate compounds. Decomposition of these intermediate compounds to corresponding oxides (MgO and Al_2O_3) or their interaction to form $MgAl_2O_4$ would be accompanied by unusual LOI values. Particle size distribution (table 2) of both types of precursors indicates agglomeration, and the particles are of micron order. Obviously, it is expected that further processing of the MAH powders could break the agglomerates to sub-micron or nano level.

3.1 *DTA studies*

MAH precursor is expected to undergo thermochemical changes during heat treatment. TGA, DTGA and DTA of MAH powder (type B) have recently been reported (Pal *et al* 2008). For comparison of thermal behaviour of types A and B precursors, their DTA curves have been incorporated in figure 1. Although, both the curves have similar nature of endothermic peaks, the number of peaks in type A is less and also they are more defined than type B. Both the curves do not exhibit endothermic peaks at ~230°C and ~400°C, and this indicates that they do not contain individual aluminium and magnesium hydroxides (Kim and Saito 2000; Yong and Wang 2002). Endothermic peaks of type A (298°C) and type B (326°C) mostly correspond to hydrate of aluminium, probably consisting of some foreign ions from parent solution.

Furthermore, many high temperature endothermic peaks (up to 1100°C) appear in both the types of precursors. This suggests that Mg^{2+} along with Al^{3+} forms intermediate hydrates which do not decompose completely even at 1000°C. It can be interpreted that this specific behaviour of MAH may be due to the absorption of Cl^-, SO_4^{2-} and NH_4^+ ions in its agglomerated structure during its preparation by fast precipitation. Thus it may be su-
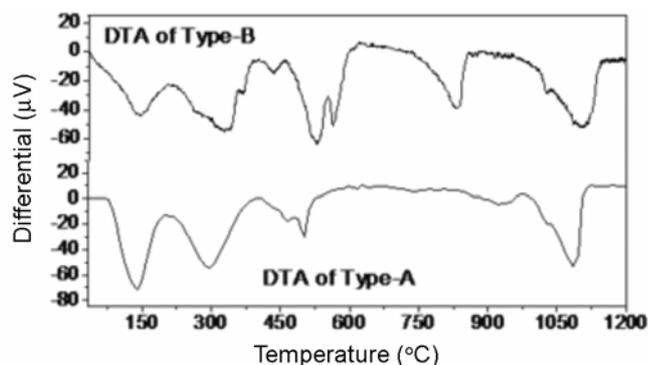
ggested that the formation of aluminium hydrate and double hydrate of magnesium and aluminium as reported (Bratton 1968) took place in the present work, however, the hydrates are complex in nature.

3.2 *Stoichiometry of MAH*

During calcination it has been observed that powders of both the processes emit considerable amount of white fumes due to structural decomposition of complex hydrates. Mukherjee (1968) also reported that calcination of MAH under vacuum evolved white vapours containing Al^{3+} ions, and the stoichiometric composition converted to MgO enriched spinel. It is expected that there would be loss of Al^{3+} or Mg^{2+} ions during calcination. In the present work, the effect of calcination techniques on stoichiometry of $MgAl_2O_4$ has been investigated.

3.3 *XRD interpretation*

XRD curves of low temperature (600°C, 2 h) calcined powders for both the methods in figure 2 indicate the formation of some crystalline intermediate compounds which are different from Mg–Al spinel or γ-Al_2O_3. These compounds retain their identity even at 900°C (figure 2). At 1000°C, the intermediate compounds decompose into Mg–Al spinel, periclase (MgO) and some intermediate phases (figure 3). It may be noted that even after 2 h soaking at 1000°C, decomposition of the complex compounds is not complete. Formation of Mg–Al spinel and
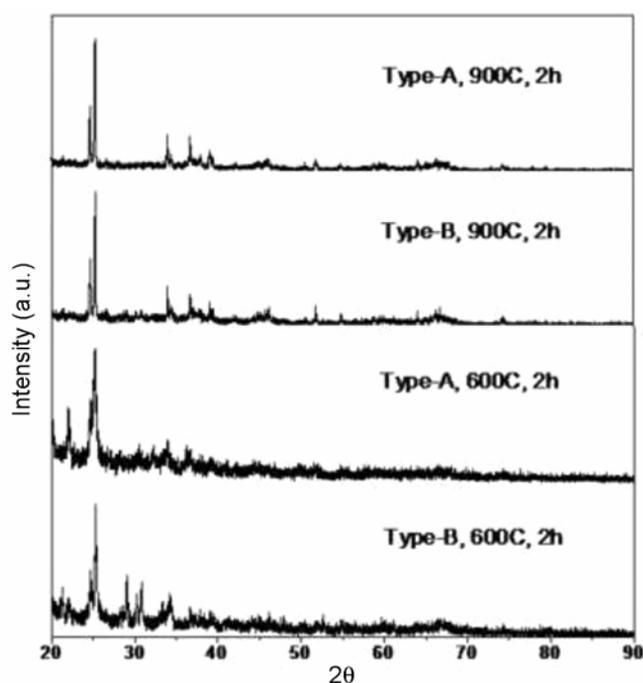
Figure 1. DTA of types A and B MAH precursors (1200°C).

Figure 2. XRD of types A and B MAH powders at 600°C and 900°C (CuK_α radiation).

periclase at 1000°C indicates double hydrate concept introduced by Bratton (1968). However, thermal stability of the double hydrate even at 900°C suggests that the double hydrate contains some foreign ions such as Cl^-, NH_4^+, SO_4^{2-} and forms a complex. Peaks of γ-Al_2O_3 at 1000°C are not visible as it forms solid solution with $MgAl_2O_4$. At temperatures ≥ 1200°C, $\gamma \rightarrow \alpha$ phase transformation of alumina takes place resulting in exsolution of corundum (α-Al_2O_3) from Mg–Al spinel structure. Then the exsolved alumina reacts with periclase to form secondary spinel. Secondary spinel formation depends on calcination temperature, in general and size of the agglomerates, in particular. It has been observed that even at 1300°C (figures 4 and 5), spinellization by interaction of MgO and Al_2O_3 is not complete, since the precipitated α-Al_2O_3 from spinel structure can not completely come into contact with MgO due to large agglomerated size of MAH powder initially taken. Comparison of present work (pilot plant level) with previous laboratory level investigation related to

development of various phases during calcination at different temperatures has been incorporated in table 3. Similar to present investigation, both the researchers (Mukherjee 1968; Bhattacharya and Samaddar 1978) had reported periclase ($d_{hkl} = 2.10$ Å) at different temperatures along with α-Al_2O_3. At low temperatures (≤ 1000°C), Mukherjee (1968) reported an unidentified phase ($d_{hkl} = 2.90$ Å) with maximum intensity and this suggests the formation of intermediate compound that does not decompose at 1000°C with 2 h soaking.

Effect of large agglomerate size is clear when XRD curves of MAH lumps calcined at further higher temperature i.e. 1400°C, 2 h (figure 6) show poor spinellization. Figure 7 reveals the XRD curves of flash calcined (900°C, 2 h) powders for both the types at 1300°C, 2 h. Both the curves contain spinel and corundum peaks indicating loss of Mg^{2+} ions during flash calcination at 900°C.

Phase quantification of the calcined powders (≥ 1200°C) was carried out by Rietveld analysis and the results have been incorporated in table 4. The results of normal calci-
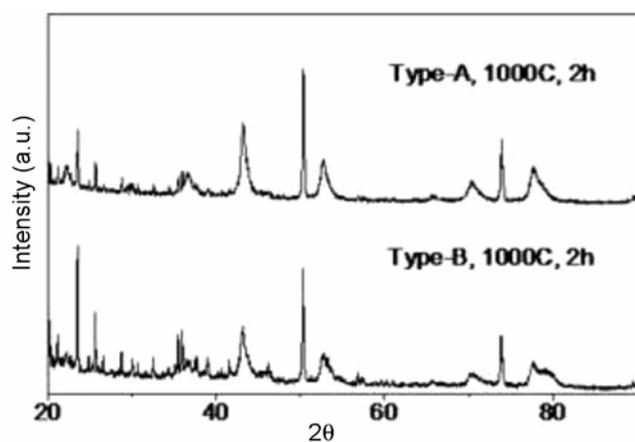

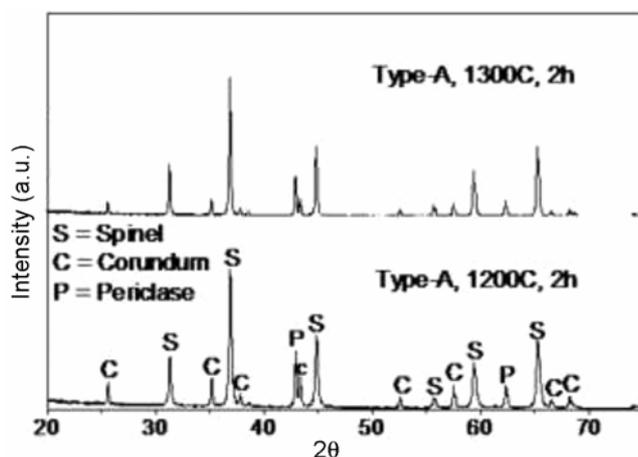**Figure 3.** XRD of types A and B MAH powders at 1000°C (CoK_α radiation).

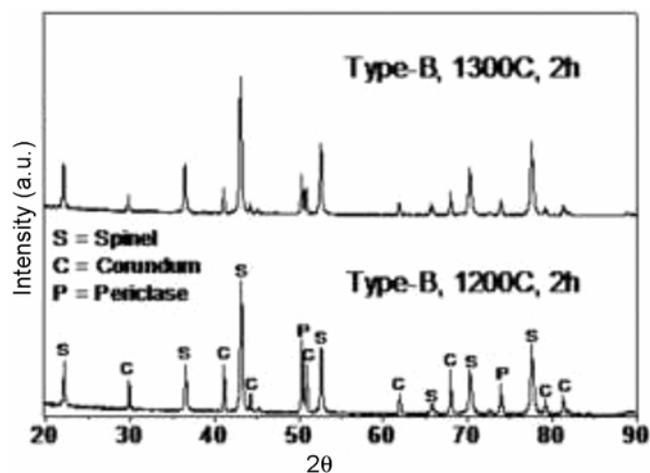**Figure 5.** XRD of type B MAH powder at 1200° and 1300°C (CoK_α radiation).

Figure 4. XRD of type A MAH powder at 1200° and 1300°C (CuK_α radiation).

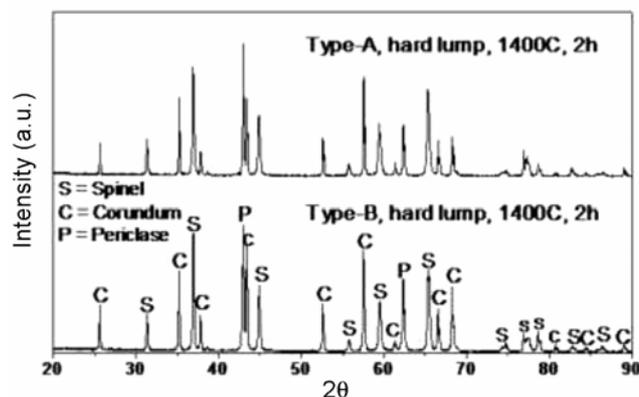**Figure 6.** XRD (hard lump) of types A and B MAH powders at 1400°C (CuK_α radiation).

Table 3. Comparison of interplanar spacing of some peaks of calcined MAH powder (present and previous works).

Mukherjee (1968)						Bhattacharya *et al* (1978)*				Present work (type B)					
800°C		1000°C		1350°C		1100°C		1200°C		900°C		1000°C		1200°C	
d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0
				4·67	10	4·607	VW	4·605	W			5·445	32		
												4·398	94	4·653	33
												4·04	40		
3·78	20	3·78	10												
										3·604	53				
										3·523	100				
2·90	100	2·90	100									2·901	32		
						2·806	W	2·821	M					2·851	35
				2·601	10					2·634	32				
2·56	30	2·57	20					2·562	VW					2·546	22
2·43	30	2·43	80	2·43	100	2·400	M	2·398	VS	2·445	31	2·432	45	2·432	100
2·10	30	2·10	30	2·102	50	2·092	VW	2·105	S			2·107	100	2·104	28
														2·082	24
						1·984	M	1·990	S	2·017	11	2·023	19	2·017	50
1·81	20	1·81	10												
1·78	20	1·77	10	1·757	20					1·762	19			1·738	11
1·70	30	1·70	20												
				1·65	10	1·633	W	1·631	W					1·648	6
														1·600	18
1·55	10	1·55	40	1·553	50			1·535	S					1·554	30
														1·489	11
1·43	20	1·43	40			1·399	M	1·412	VS	1·410	18	1·429	17	1·427	52
														1·403	7
				1·365	10									1·373	11

*W, weak; VW, very weak; M, medium; S, strong; VS, very strong.

Table 4. Phase composition of MAH precursors (types A and B) calcined at different temperatures under various process conditions.

Sample details	Temp. (2 h)	Phase composition of type A					Phase composition of type B				
		$MgAl_2O_4$	$\alpha\text{-}Al_2O_3$	MgO	$MgO:Al_2O_3$	%Wt loss (Al_2O_3/MgO)	$MgAl_2O_4$	$\alpha\text{-}Al_2O_3$	MgO	$MgO:Al_2O_3$	%Wt loss Al_2O_3/MgO
Powder (normal calcination)	1200°C (agated)	72·7	15·5	11·8	1·212 : 1	17·51 (Al_2O_3)	72·5	17·0	10·5	1·139 : 1	12·18 (Al_2O_3)
	1300°C (agated)	77·0	13·8	9·2	1·137 : 1	12·06 (Al_2O_3)	77·4	13·0	9·6	1·165 : 1	14·16 (Al_2O_3)
Lump (normal calcination)	1400°C (agated)	44·1	31·0	24·9	1·511 : 1	33·82 (Al_2O_3)	39·0	40·1	20·9	1·188 : 1	15·81 (Al_2O_3)
Powder (flash calcination at 900°C, 2 h)	1300°C (agated)	88·9	11·1	–	0·851 : 1	14·84 (MgO)	86·5	13·2	0·3	0·835 : 1	16·52 (MgO)

nation powders indicate increased spinellization for both the processes with higher calcination temperatures. But for coarser agglomerates (lumps), spinellization is delayed even at 1400°C. From this, it can be interpreted that primary spinel formation by the decomposition of intermediate double hydrate is not dependent on the size of agglomerates. However, in secondary spinel formation, MgO produced has to come into contact with alumina and therefore, spinellization in case of coarser agglomerates gets restricted. From phase compositions of $MgAl_2O_4$, MgO and Al_2O_3 by Rietveld analysis, mass balance was done to estimate the molar ratio of $MgO:Al_2O_3$ in calcined powders. Furthermore, with this molar ratio, percent wt loss of either Al_2O_3 or MgO was calculated (table 4). In case of normal heat treatment route, Al_2O_3 loss has been observed in both the types of powders, and it
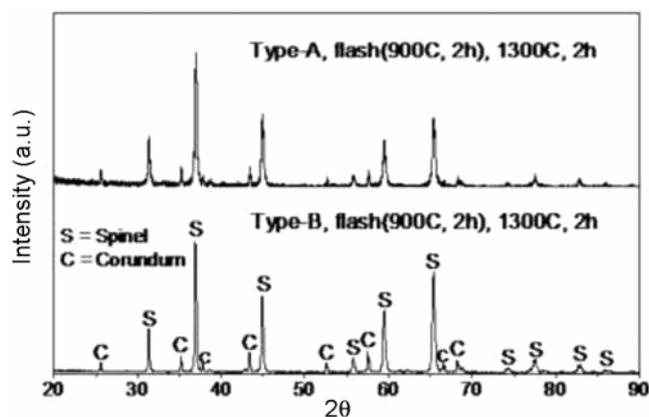
Figure 7. XRD of flash calcined (900°C, 2 h) types A and B MAH powders at 1300°C (CuK$_\alpha$ radiation).

increases with the size of the agglomerates. Again, MgO loss occurred for flash calcined powders resulting in alumina enriched spinel. Further in depth investigation may be necessary to establish the reasons of either Al$_2$O$_3$ or MgO loss during different modes of calcination of MAH precursors.

4. Conclusions

From the present work, following conclusions can be drawn:

(I) Precursors formed by both the processes (types A and B) convert to some intermediate compounds which are thermally stable even at 900°C. Thus spinel formation gets restricted at low temperatures.

(II) Although major decomposition of the intermediate compounds starts at 1000°C, it is not complete at this temperature. Decomposition is accompanied by the formation of MgO and spinel phases. The alumina present at 1000°C exists as solid solution with spinel.

(III) At $\geq$ 1200°C, decomposition of the complexes is complete forming MgO and spinel. Alumina which was present as solid solution in spinel structure separates out as α-Al$_2$O$_3$, and it interacts with MgO to form secondary spinel. However, effect of agglomeration is detrimental for this MgO and Al$_2$O$_3$ interaction, and the formation of spinel gets restricted.

(IV) Mode of heat treatment has effect on stoichiometry of spinel. Normal heating causes loss of Al^{3+} ions forming magnesia enriched spinel, whereas flash calcination effects loss of Mg^{2+} ions resulting in alumina enriched spinel.

References

Bailey J T and Russell R J R 1968 *Ceram. Bull.* **47** 1025
Bakker W T and Lindsay J G 1967 *Am. Ceram. Soc. Bull.* **46** 649
Behera S K, Barpanda P, Pratihar S K and Bhattacharya S 2004 *Mater. Lett.* **58** 1451
Bhattacharya Hemanta and Samaddar B N 1978 *J. Am. Ceram. Soc.* **61** 279
Bickmore C R, Waldner K F, Treadwell D R and Laine R M 1996 *J. Am. Ceram. Soc.* **79** 1419
Bratton R J 1968 *Am. Ceram. Soc. Bull.* **48** 759
Delau J G M 1970 *Am. Ceram. Soc. Bull.* **49** 572
Katanic-Popovic J, Miljevic N and Zec S 1991 *Ceram. Int.* **17** 49
Kim W and Saito F 2000 *Powder Technol.* **113** 109
Lepkova D, Bartarjav A, Samuneva B, Ivanova Y and Georgieva L 1991 *J. Mater. Sci.* **26** 4861
Li J -G, Ikegami T, Lee J -H, Mori T and Yajima Y 2001 *J. Eur. Ceram. Soc.* **2** 139
Mukherjee S G 1968 *Spinel formation from co-precipitated magnesium with hydrous aluminium oxide*, Ph D Thesis, Banaras Hindu University, Varanasi
Mukherjee S G and Samaddar B N 1966 *Trans. Ind. Ceram. Soc.* **25** 33
Pal Soumen, Bandyopadhyay A K and Pal P G 2008 *Trans. Ind. Ceram. Soc.* **67** 203
Samaddar B N, Paul P G and Bhattacharya Hemanta 1979 *Trans. Ind. Ceram. Soc.* **38** 151
Singh V K and Sinha R K 1997 *Mater. Lett.* **31** 281
Suyama Y and Kato A 1982 *Ceram. Int.* **8** 17
Ye Guotian, Oprea George and Troczynski Tom 2005 *J. Am. Ceram. Soc.* **88** 3241
Yong C C and Wang J 2002 *J. Am. Ceram. Soc.* **84** 1225