Enhancement of MgAl$_2$O$_4$ spinel formation from coprecipitated precursor by powder processing

SOUMEN PAL*, A K BANDYOPADHYAY, S MUKHERJEE[†], B N SAMADDAR[††] and P G PAL

Department of Ceramic Technology, Government College of Engineering and Ceramic Technology, Kolkata 700 010, India

[†]School of Materials Science and Nanotechnology, Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata 700 032, India

[††]Ex-emeritus Professor (AICTE), Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata 700 032, India

Abstract. Although low temperature fast coprecipitation technique has been used to synthesize stoichiometric (MgO–nAl$_2$O$_3$, $n = 1$) MgAl$_2$O$_4$ spinel forming precursor, delayed spinellization has always been the concern in this process. In this article, the precursor of this 'fast technique' has been used for bulk production by further processing by high speed mixing with solvents and mechanical activation by attrition milling in terms of superior spinellization. At 1000°C, MgAl$_2$O$_4$– γ-Al$_2$O$_3$ solid solution and MgO phases are formed (spinel formed by 1000°C is regarded as primary spinel). At higher temperatures, due to large agglomerate size, MgO can not properly interact with the exsolved α-Al$_2$O$_3$ from spinel solid solution to form secondary spinel; and consequently spinellization gets affected. Solvent treatment and attrition milling of the coprecipitated precursor disintegrate the larger agglomerates into smaller size (effect is more in attrition). Then MgO comes in proper contact with exsolved alumina, and therefore total spinel formation (primary + secondary) is enhanced. Extent of spinellization, for processed calcined samples where some alumina exists as solid solution with spinel, can be determined from the percentage conversion of MgO. Analysis of the processed powders suggests that the 4 h attrited precursor is most effective in terms of nano size (< 25 nm) stoichiometric spinel crystallite formation at ≤ 1100°C.

**Keywords.** MgAl$_2$O$_4$ spinel; coprecipitation technique; mixing; milling; phase transformation.

1. Introduction

Technology transfer from laboratory level to pilot plant level and subsequently its scaling upto bulk production by suitable design of process flow chart is the primary objective for any successful research work. To achieve multi-component oxides with defined stoichiometry, coprecipitation is a simple and unique technique. Among all wet chemical routes for synthesis of multi-component oxides, coprecipitation is one of the oldest (Mukherjee and Samaddar 1966; Bratton 1969) and this process attracted huge interests among scientists (Samaddar *et al* 1979; Gusmano *et al* 1991; Katanic-Popovic *et al* 1991; Samaddar 1995). The processes introduced by Mukherjee and Samaddar (1966), its scaling upto both continuous (Samaddar *et al* 1979) and batch (Samaddar 1995) processes with certain modifications, and by Bratton (1969) were successful in achieving precursors with spinel

(MgAl$_2$O$_4$) stoichiometry. Methodology of conversion of precursor hydrate was not adequately pointed out by the authors (Mukherjee and Samaddar 1966) and they did not report complete spinellization even at 1100°C.

Hemanta Bhattacharya and Samaddar (1978) reported the formation of a non-stoichiometric spinel when the coprecipitated powder was calcined at 1100°C. Recent work (Soumen Pal *et al* 2010) indicates that bulk production of precursor powder by the fast coprecipitation technique at low temperatures (Samaddar 1995) has spinel stoichiometry (MgO–nAl$_2$O$_3$, $n = 1$). However, during its subsequent calcination, $n = 1$ could not be retained and in addition spinellization got delayed. During this fast process, it is expected that the precursor gel would be highly agglomerated. Furthermore, the gel may absorb ions such as Cl$^-$, SO$_4^{2-}$ and NH$_4^+$. To support this view, as an example, it may be mentioned here that metallurgy grade technical alumina formed by Bayer's process remains highly agglomerated and also absorbs reasonable amount of Na$^+$ ions from mother liquor. The absorbed Na$^+$ ions exist as β-Al$_2$O$_3$ in the calcined alumina powder. By proper

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*Author for correspondence (soumenpal12@gmail.com)
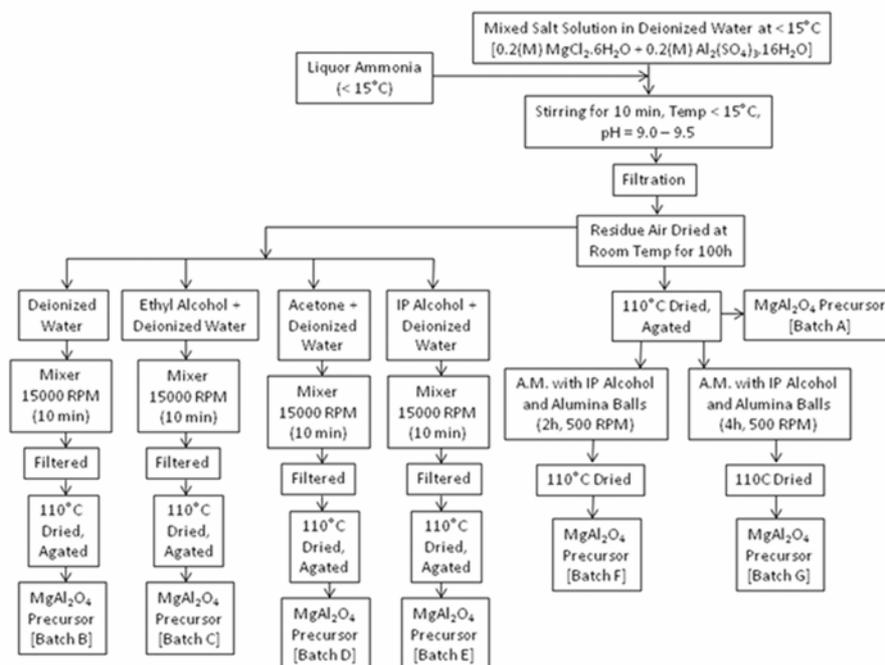
Figure 1. Flow chart depicting the preparation procedure of processed spinel precursors through coprecipitation technique.

process manipulation such as control of precipitation rate, adjustment of pH value and use of dispersing agents etc, it is possible to prepare submicron or even nano level alumina powders with high purity i.e. >99·9% (Flock 1978). In another study, Paul and Samaddar (1984) reported that technical alumina available in the market can be processed to develop submicron interactive alumina powder.

In the recent reporting (Soumen Pal *et al* 2010), it is demonstrated that 100% spinellization by the fast technique (Samaddar 1995) cannot be achieved even at 1300°C mainly because of agglomeration. To achieve reduction of agglomerate size in order to enhance spinel formation had been the reason for examining precipitate washing and comminution in the present work. Here the precursor hydrate is treated with different solvents in the first set of experiments, and attrited to study the effect of mechanical activation in the second set of investigations.

2. Experimental

2.1 *Materials*

Analytical reagent (AR) grade magnesium chloride, aluminium sulphate, liquor ammonia and different organic solvents such as ethyl alcohol, acetone and isopropyl alcohol were used as raw materials. 100 l of mixed

salt solution in deionized water having strength 0·2 M with respect to both magnesium chloride and aluminium sulphate was used in a reactor and the solution temperature was maintained at <15°C (Samaddar 1995). Measured amount of liquor ammonia was added in the mixed solution rapidly followed by vigorous stirring for 10 min to maintain pH in the range 9–9·5 during coprecipitation. As liquor ammonia was added at once to attain desired pH range, the process was regarded as 'fast' compared to other procedures (Bratton 1969; Gusmano *et al* 1991; Katanic-Popovic *et al* 1991). The white gelatinous precipitate was filtered and 'air dried' (30°C) for 100 h. The 'cake' type gel was stored in sealed containers.

Seven batch compositions as depicted in figure 1 show the treatment done for each of the batch precursor powders. For powder B, 200 g coprecipitated gel was treated with 400 ml deionized water. In case of powders C, D and E, 200 g gel was mixed with 200ml organic solvent + 200 ml deionized water. Stabilized toughened cubic zirconia pot was used in the attritor (Model–01 HD/01 HDDM, Union Process Ltd., USA). To ascertain whether longer duration of attrition reduces the particle size of the coprecipitated material, in three separate batches, dried and agated powders were attrited for 6, 8 and 10 h respectively. However, the particle size distribution (not included) of these powders did not improve significantly in comparison with the 4 h attrited (batch G) material. Hence, attrition milled batches of higher durations were not considered.

2.2 *Characterization of precursors*

Chemical analysis of the powders was carried out by wet chemical method to estimate MgO and Al_2O_3 on loss free basis. Particle size distribution of untreated, representative solvent treated and attrited (dried and calcined) powders was determined by Nano-Sizer (ZetaSizer Nano-S, Model-Zen 1600, Malvern, USA) with laser beam technique using sodium hexametaphosphate as dispersing agent. To assess the spinel formation, precursors were heat treated at 1000°C, 1100°C and 1200°C with varying soaking times (2–3 h) depending on the attainment of constant weight. XRD (PW 3050/60 Goniometer, PANalytical, Netherlands) spectral patterns were recorded using CuK_α and CoK_α radiations depending on availability. Crystallite size of the powders heat treated at 1000°C for 3 h were determined by Scherrer equation (Cullity 1959). To confirm the size from Scherrer equation, BET specific surface area of the same powders were measured (Model–SORPTY 1750, CARLO ERBA Strumentazione, Italy) and equivalent spherical crystallite size determined. To verify the morphology of the powders, representative samples were viewed under scanning electron microscope (QUANTA 200 MK2 with EDS attachment, FEI, Netherlands). HR-TEM (JEOL–2100, Japan) images of the most effective spinel forming powder (G; 1000°C for 3 h and 1100°C, 3 h) were recorded to ascertain the identity of individual crystallites in the agglomerates.

3. Results and discussion

3.1 *Chemical analysis and particle size distribution*

Chemical analysis (table 1) reveals that $Al_2O_3 : MgO$ molar ratio of solvent treated and attrited precursors does not change appreciably from untreated gel. Considerable difference in LOI values can be seen among solvent treated and attrited powders. Probably, this difference could be due to the extent of removal of physically bound water molecules and absorbed foreign ions viz. Cl^-, SO_4^{2-} and NH_4^+ from agglomerated materials. Particle size dis-
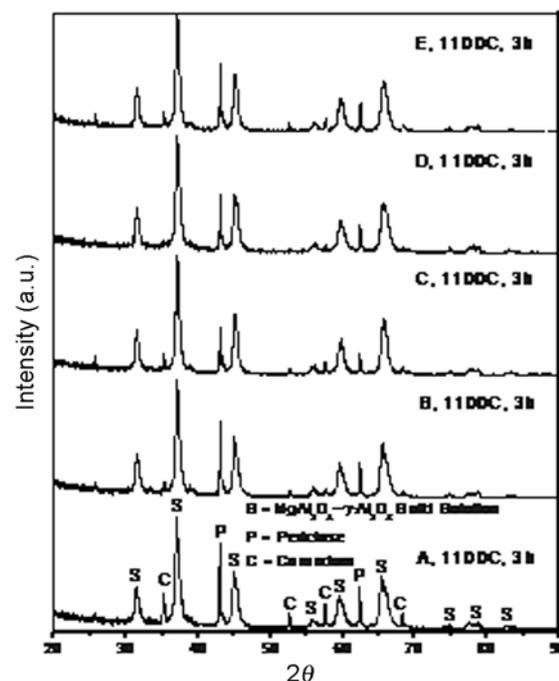
tribution (table 2) indicates that untreated precursor can be dispersed to micron level by magnetic stirring in presence of sodium hexametaphosphate as dispersing agent.
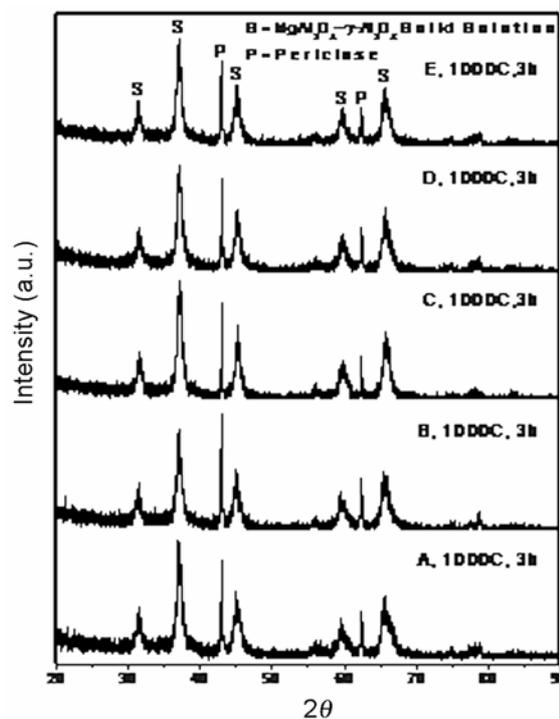

Figure 2. XRD spectra at 1000°C (3 h) of powders A, B, C, D and E. Unconverted alumina (γ-Al_2O_3) exists as solid solution with $MgAl_2O_4$.

Figure 3. XRD spectra at 1100°C (3 h) of powders A, B, C, D and E. Compared to 1000°C (3 h) XRD spectra, exsolution of corundum from spinel solid solution has occurred to a certain extent.

Table 1. Chemical analysis of the precursor powders dried at 110°C.

| Powder (Batch) | Wt% | | Wt% L.O.I (1200°C, 2 h) | Molar ratio ($Al_2O_3 : MgO$) |
	Al_2O_3	MgO		
A	21·93	8·60	69·32	1·008 : 1
B	30·46	11·96	57·48	1·007 : 1
C	33·89	13·28	52·69	1·009 : 1
D	32·17	12·58	55·14	1·011 : 1
E	31·22	11·58	57·04	1·066 : 1
F	26·07	10·25	63·51	1·006 : 1
G	24·66	9·71	65·50	1·004 : 1

Table 2.   Particle size distribution of a few representative powders.

Size (dia. in nm)	Mean volume (%)					
	110°C dried				1000°C, 3 h	
	A	E	F	G	F	G
342·0	–	–	–	–	–	–
396·1	–	–	–	18·3	–	–
458·7	–	–	–	46·8	–	7·6
531·2	–	–	–	34·9	–	34·5
615·1	–	34·6	54·2	–	20·8	40·7
712·4	–	46·8	45·8	–	49·8	17·2
825·0	–	18·6	–	–	29·4	–
955·4	–	–	–	–	–	–
1106·0	–	–	–	–	–	–
1281·0	–	–	–	–	–	–
1484·0	–	–	–	–	–	–
1718·0	51·7	–	–	–	–	–
1990·0	48·3	–	–	–	–	–
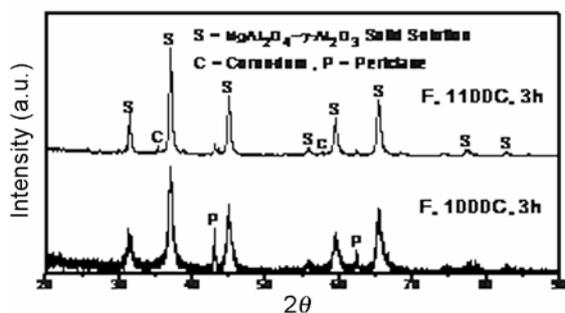
Figure 4.   XRD spectra of powder F calcined at 1000°C (3 h) and 1100°C (3 h).
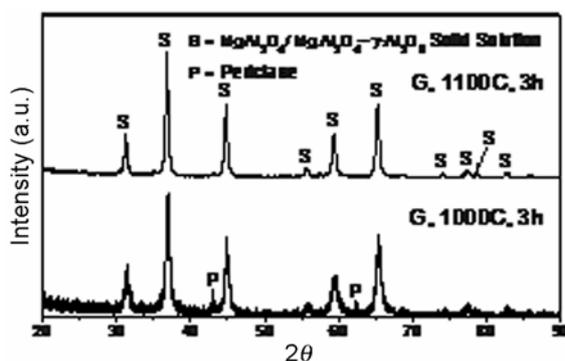
Figure 5.   XRD spectra of powder G calcined at 1000°C (3 h) and 1100°C (3h).

Solvent treated and attrited powders remain in sub-micron order. Further, in most cases, a large fraction of the powders remains within a narrow range of size.

3.2   *Phase analysis by XRD spectra*

X-ray diffraction studies (figures 2–5 and 9) of untreated, solvent treated and attrited precursors, heat treated at dif-
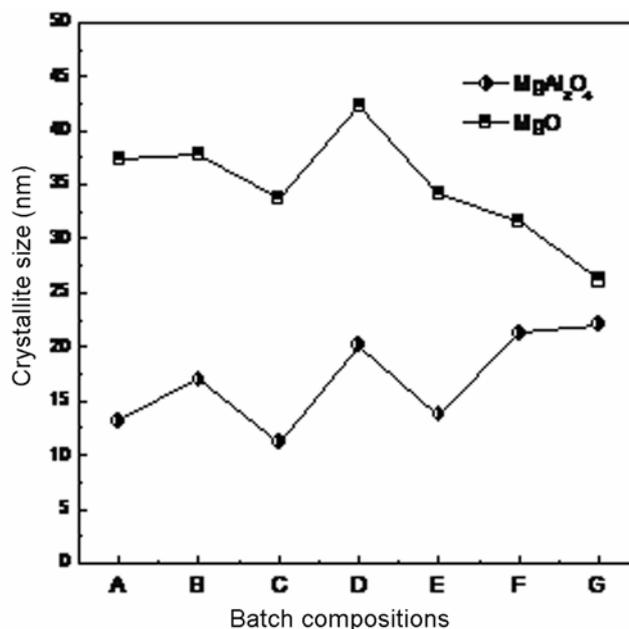
Figure 6.   Calculated crystallite size (by Scherrer equation) of processed powders calcined at 1000°C (3 h) from XRD peaks of $MgAl_2O_4$ and MgO.

ferent temperatures, reveal the phases at the corresponding temperatures. Analysis of XRD spectra of all the powders calcined at 1000°C, 3 h (figures 2, 4, 5) reveals formation of $MgAl_2O_4$–γ-Al_2O_3 solid solution and MgO. It is to be noted that γ-Al_2O_3, equivalent to wt% MgO in table 4 (i.e. for stoichiometric spinel formation), undergoes solid solution with the primary spinel formed and therefore we obtain only non-stoichiometric spinel and MgO phases at 1000°C (3 h). Change in d_{hkl} values of $MgAl_2O_4$ (table 3) in the 1000°C, 3 h calcined powders shows the existence of non-stoichiometry resulting from $MgAl_2O_4$–γ-Al_2O_3 solid solution. It may be noted that this type of $MgAl_2O_4$–γ-Al_2O_3 solid solution has been

reported by authors investigating with alumina enriched spinel (Jing Shou-Yong *et al* 2000; Zawrah 2004), where only non-stoichiometric spinel was stated in the XRD analysis at ≤1080°C. In another work, Suwa *et al* (1986) reported γ-Al$_2$O$_3$–MgAl$_2$O$_4$ solid solution phase in the range 500–1025°C, when they heat treated gels with a ratio of 93 wt% Al$_2$O$_3$ to 7 wt% MgO. They also revealed phase separation of α-Al$_2$O$_3$ from γ-Al$_2$O$_3$–MgAl$_2$O$_4$ solid solution at 1100°C, and achieved 100% separation at this temperature in presence of 0·5 wt% α-Al$_2$O$_3$ seeds.

Compared to 1000°C, spinellization increases at 1100°C, 3 h (figures 3–5) in the powders. At this temperature, some γ-Al$_2$O$_3$ which was in solid solution with primary spinel at 1000°C, undergoes phase transformation to α-Al$_2$O$_3$ and exsolves out from spinel solid solution (in the powders A, B, C, D, E and F complete exsolution does not occur at 1100°C). Thereafter, secondary spinel is formed by the interaction of exsolved α-Al$_2$O$_3$ and MgO. Spinel formation is very high in the

Table 3. Effect of MgAl$_2$O$_4$–γ-Al$_2$O$_3$ solid solution on d_{hkl} values of stoichiometric MgAl$_2$O$_4$ ($d_{113} = 2\cdot43215$)* in the 1000°C, 3 h calcined powders.

Batch	d_{113} (Å)	RI	Phase identity
A	2·42793	100·00	MgAl$_2$O$_4$–γ-Al$_2$O$_3$ solid solution
B	2·42429	77·43	-do-
C	2·42218	100·00	-do-
D	2·42717	100·00	-do-
E	2·43024	100·00	-do-
F	2·42626	100·00	-do-
G	2·42390	100·00	-do-

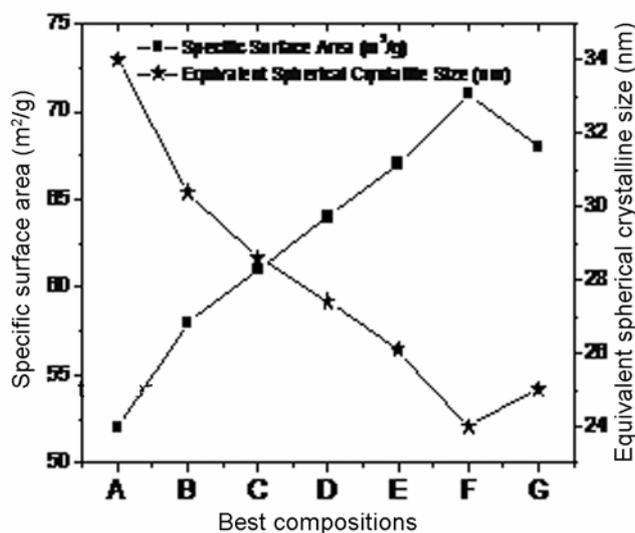*Batch G powder at 1100°C (3 h) where complete spinellization has occurred

attrited powders F and G at 1100°C (figures 4 and 5), and spectrum of G reveals only spinel phase indicating complete spinellization at this temperature. XRD patterns at 1100°C of the remaining powders (figure 3) reveal non-stoichiometric spinel as major phase along with some MgO and α-Al$_2$O$_3$.

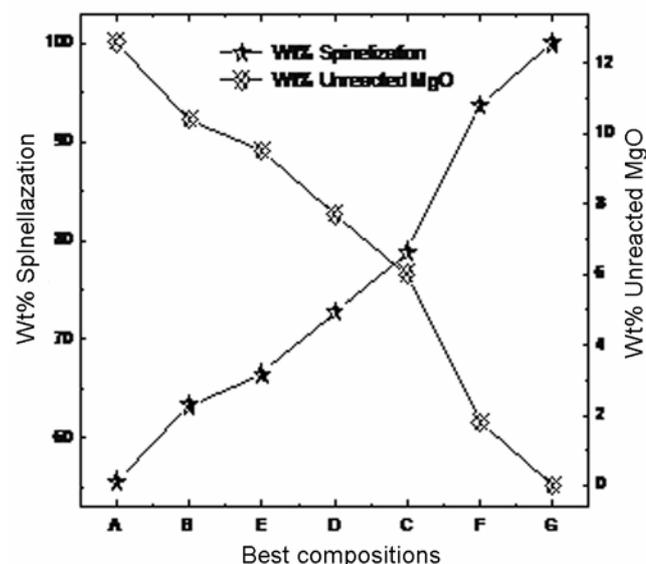Average crystallite size at 1000°C, 3 h (figure 6) has been calculated using Scherrer equation (Cullity 1959)

Figure 8. Graph revealing unconverted MgO as index for MgAl$_2$O$_4$ formation in the processed powders calcined at 1100°C (3 h).


Figure 7. BET specific surface area and equivalent spherical crystallite size of 1000°C (3 h) heat treated powders.
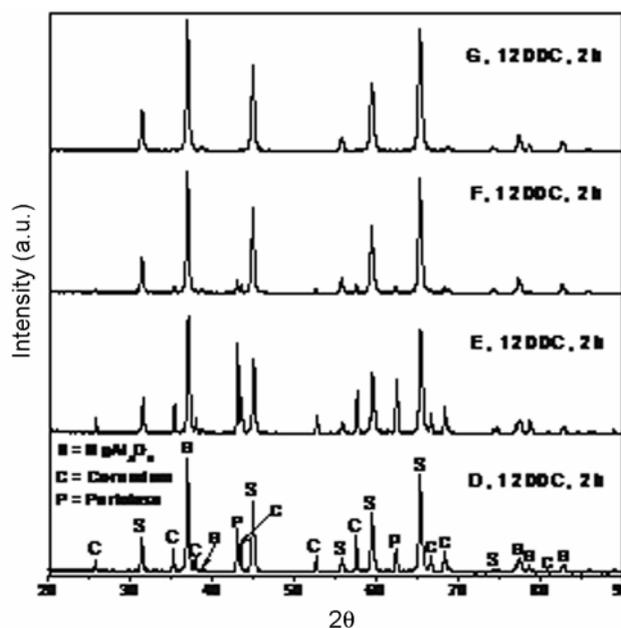
Figure 9. X-ray diffraction spectral patterns of powders D, E, F and G heat treated at 1200°C (2 h).

Table 4. Phase quantification (by Rietveld analysis) of powders at different calcination temperatures.

Sample identity	Temp. with dwell time	Phase quantification (wt%)		
		$MgAl_2O_4$	α-Al_2O_3	MgO
A	1100°C, 3 h	78·6	8·8	12·6
	1200°C, 3 h	72·5	17·0	10·5
B	1100°C, 3 h	86·9	2·7	10·4
C	1100°C, 3 h	89·3	4·6	6·0
D	1100°C, 3 h	92·3	–	7·7
	1200°C, 2 h	77·5	16·1	6·4
E	1100°C, 3 h	86·1	4·4	9·5
	1200°C, 2 h	71·2	20·6	8·2
F	1000°C, 3 h	93·7	–	6·3
	1100°C, 3 h	95·7	2·5	1·8
	1200°C, 2 h	96·9	2·2	0·9
G	1000°C, 3 h	98·0	–	2·0
	1100°C, 3 h	100·0	–	–
	1200°C, 2 h	100·0	–	–
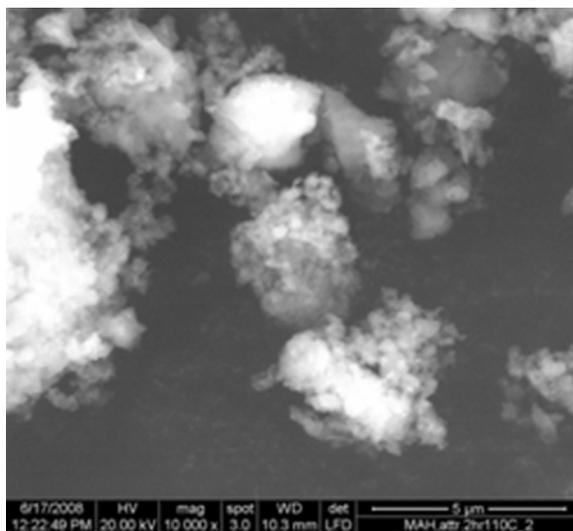
Figure 10. Scanning electron microscope image revealing similar morphology of the powders heat treated at different temperatures.

i.e.

$$D(nm) = \frac{0·89\lambda}{B\cos\theta},$$

where D is average crystallite size, λ is wavelength of radiation, θ the Bragg angle and B the broadening of diffraction line measured at half maximum intensity. Figure 6 shows that each powder contains nano size crystallites, and this suggests that the present coprecipitation technique can evolve nanocrystallites. Crystallite size has also been verified by BET technique. BET specific surface area of all the 1000°C, 3 h calcined powders were measured, and from those values equivalent spherical crystallite size (figure 7) were determined.

Phase quantification results by Rietveld analysis (table 4) indicate that extent of spinel formation is process dependent (although data for all the powders at 1000°C, 1100°C and 1200°C have not been incorporated, the listed ones are sufficient for interpretation). From wt% conversion of MgO (i.e. 28·33 minus wt% MgO in table 4), wt% actual spinellization at 1100°C, 3 h has been determined and incorporated in figure 8. Complete spinellization of the powder G at 1100°C, 3 h suggests that the agglomerate size reached optimum fineness where adequate contact between periclase and alumina occurred. Figure 8 shows that compared to the untreated gel, treatment with organic solvents also increases spinellization moderately. An important observation is that in the powders heat treated at 1100°C, 3 h, wt% spinellization values in figure 8 may not match with the ones in table 4. This is because when some amount of alumina remains in spinel as solid solution, Rietveld analysis will show higher wt% spinel value than actual spinellization. So, wt% $MgAl_2O_4$ at 1100°C, 3 h in table 4 does not indicate actual spinellization for the powders A, B, C, D, E and F. Figure 9 shows the diffraction patterns of the representative samples calcined at 1200°C, 2 h (as CoKα radiation was used for powder A, its curve has not been included for the sake of uniformity). In most powders, spinellization increases at 1200°C (2 h), compared to 1100°C (3 h), due to higher secondary spinel formation. From wt% conversion of MgO in table 4, wt% actual spinellization can also be determined at 1200°C, 2 h (not included). Major exsolution of α-Al_2O_3 from spinel solid solution occurs in all the powders at 1200°C (2 h), however, extent of secondary spinel formation depends on fineness of the material.

3.3 *Microstructure*

As particle size distribution (table 2) of the powders does not differ in a broad way (most of the powders are in submicron size), SEM images revealed somewhat similar
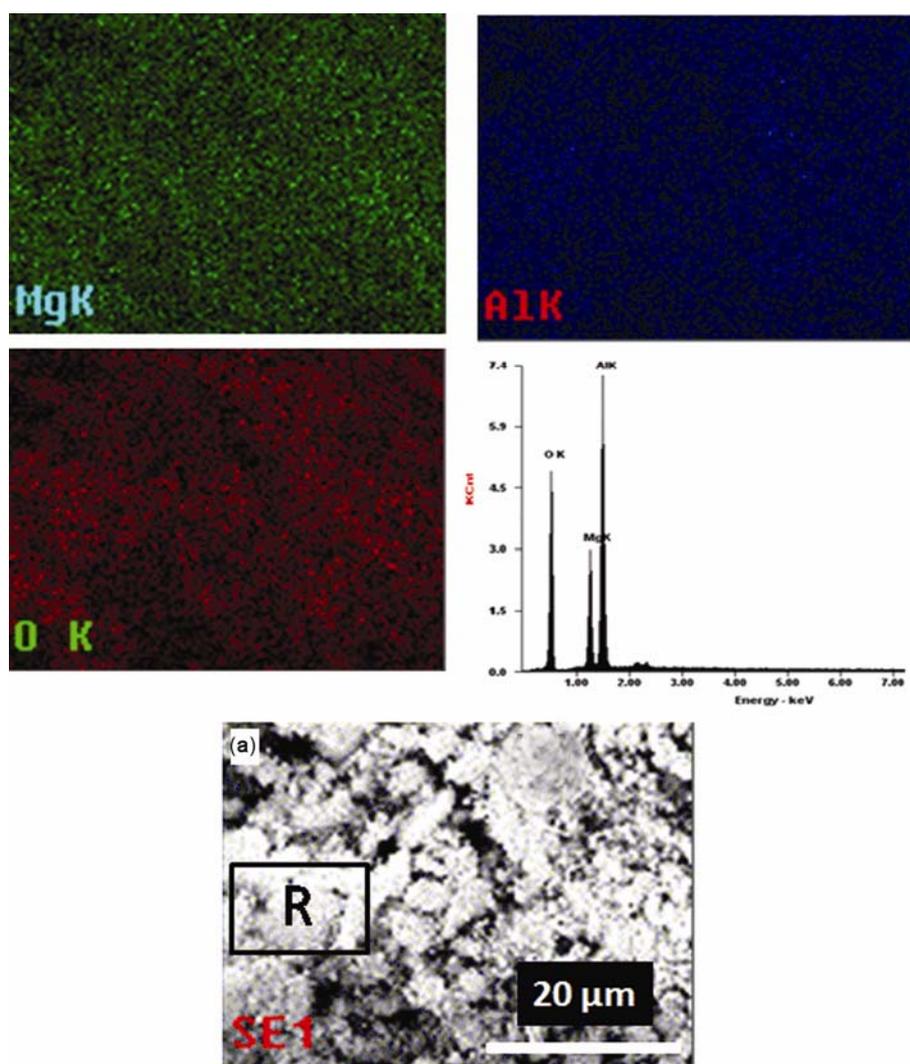
Figure 11. Distribution of elements magnesium, aluminium and oxygen in 1000°C (3 h) heat treated powder G i.e. image (a). The EDS is of region R.

morphological trend. As powder G is the most effective precursor in terms of spinellization at ≤ 1100°C, it has been considered as the representative sample for microstructure studies. For image of the 110°C dried representative precursor, powder F has been viewed.

Shape of the agglomerates and their substructure were similar in the temperature range 110–1100°C, and the same can be observed in figure 10. Elemental mapping of 1000°C, 3 h and 1100°C, 3 h heat treated materials showed the presence of only Mg, Al and O, and in them the approximate atomic ratio of Mg : Al was 1 : 2. This ratio indicates that spinel stoichiometry has been retained in the material. Figure 11 gives the elemental distribution and EDS spectrum of the 1000°C, 3 h calcined powder. HR-TEM photograph (figure 12a) shows the agglomerate size of the crystallites of 1000°C, 3 h powder, and this size is at par with the agglomerate (particle) size in table 2. When a certain portion of this image is viewed under high magnification (figure 12b), approximate crystallite

size of < 25 nm can be observed. Here it may be noted that there is no wide variation in crystallite size by the three techniques i.e. Scherrer equation, BET and HR-TEM. Therefore, it may be interpreted that although by further processing we can reduce the agglomerate size, the crystallite size of all the precursors broadly remains in the same range. For the representative sample G heat treated at 1100°C, 3 h (100% spinellization at this temperature), HR-TEM image (figure 12c) shows nano size crystallites and this size is at par with figure 12b. Results of HR-TEM, BET and size by Scherrer equation suggest the formation of nano size crystallites using untreated or processed precursor which was prepared by low temperature fast coprecipitation technique.

4. Conclusions

For the precursor of low temperature fast coprecipitation technique (Samaddar 1995), enhancement of MgAl₂O₄
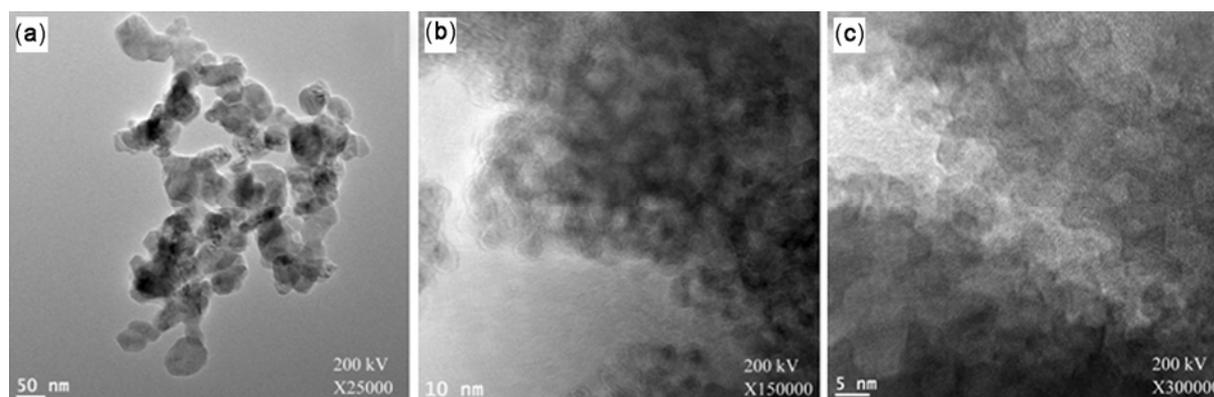
Figure 12. TEM of powder G (**a**) Size of the agglomerate at 1000°C (3h) under lower magnification; (**b**) Nano size crystallites when part of the 1000°C (3 h) calcined agglomerate, i.e. image (**a**), is viewed at higher magnification; (**c**) Nano size crystallites of spinel at 1100°C (3 h).

spinel formation has been achieved with regard to bulk production. Present investigation reveals that solvent treatment and mechanical activation of the coprecipitated material do not affect the precursor stoichiometry (MgO–nAl$_2$O$_3$, $n = 1$) appreciably. This work suggests that the material (dried and agated) when attrited for 4 h, is the most effective processed precursor to produce stoichiometric spinel containing nano size crystallites at 1100°C (3 h).

At 1000°C (3 h), MgAl$_2$O$_4$–γ-Al$_2$O$_3$ solid solution and MgO phases are formed. Phase transformation of alumina (γ to α) occurs at higher temperatures and α-Al$_2$O$_3$ exsolves out of spinel solid solution. Thereafter secondary spinel is formed by the interaction of exsolved α-Al$_2$O$_3$ and MgO.

Instead of accepting the wt% spinel formation data (Rietveld quantification) for processed calcined samples where some alumina exists as solid solution with spinel, actual wt% spinellization should be determined from wt% conversion of MgO because when some amount of alumina remains in spinel as solid solution, Rietveld analysis will show higher wt% spinel value than actual spinellization.

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