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Synthesis of Mg–Al spinel powder via precipitation using ammonium bicarbonate as the precipitant

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Abstract

A precursor for Mg–Al spinel has been synthesized via the precipitation method, using ammonium bicarbonate as the precipitant. The precursor was composed of crystalline ammonium dawsonite hydrate [$NH_4Al(OH)_2CO_3{\cdot}H_2O$] and hydrotalcite [$Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$] phases. The precursor converted to pure spinel phase at ~900°C via two steps upon calcination: (i) decomposition of hydrotalcite at lower temperatures (400–800°C) and (ii) solid-state reaction between MgO (decomposed from hydrotalcite) and γ-Al_2O_3 (derived from $NH_4Al(OH)_2CO_3{\cdot}H_2O$) at higher temperatures (>800°C). The effect of calcination temperature on particle morphology and sinterability of the resultant spinel powders were investigated.

Keywords: Calcination; $MgAl_2O_4$; Powders–chemical preparation; Sintering; Spinels

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) is an important ceramic material considering its high melting point (2135°C), high resistance against chemical attack,[1] good mechanical strength both at room temperature and elevated temperatures,[2,3] low dielectric constant,[4] and excellent optical properties.[5] Dense spinel ceramics could potentially find frequent applications in diverse engineering fields. However, since the spinellization reaction is accompanied by ~5% volume expansion,[6] dense spinel ceramics of stoichiometric composition with high-purity characteristics are difficult to fabricate directly from mixtures of individual Al_2O_3 and MgO powders via solid-state reaction using the conventional pressureless-sintering technique. In practice, dense materials are produced by a two-stage firing process: calcining the powder mixture at ~1600°C to complete the spinellization reaction, followed by ball milling and refiring at even higher temperatures.

Synthesis of highly reactive, phase-pure spinel powder seems to be a crucial step to the successful fabrication of dense ceramic materials at reasonable sintering temperatures. It is well accepted that the wet-chemical processing of multi-cation oxides provides considerable advantages of good mixing of the starting materials and excellent chemical homogeneity of the final product. In recent years, several types of wet-chemical techniques or wet-chemical related techniques have been developed and successfully used for the production of pure spinel powders at relatively low temperatures. These methods include hydroxide coprecipitation,[7–9] sol–gel of metal alkoxides or inorganic salts,[10–14] spray-drying,[15,16] freeze-drying,[17,18] modified Pechini process,[19] flame spray pyrolysis,[20] and combustion synthesis.[21] The above methods have their own respective advantages and disadvantages. For spray-drying (pyrolysis), freeze-drying, modified Pechini process and combustion synthesis, chemical composition (Mg/Al molar ratio) of the starting salt solution was easily kept to the final product. Unfortunately, the resultant spinel powders generally do not show desirable sinterability. Suyama and Kato[15] reported that the spinel powder prepared by the spray pyrolysis technique only densified to 93% of the theoretical density after pressureless sintering at 1590°C for 2 h. Spinel powders synthesized by sol–gel of metal alkoxides are usually characterized by high reactivity and less agglomeration.[10–12] However, metal alkoxides are expensive and most of the solvents for them are toxic. Besides, special measures are required during manipulating alkoxide materials due to their high sensitivity to

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the moisture in air. Precipitation using inorganic salts is a relatively convenient and cost-effective way among these wet-chemical methods. But mainly due to severe agglomeration, the spinel powder produced by hydroxide coprecipitation using ammonia water as the precipitant has not been sinterable enough to achieve full densification via pressureless sintering without additives.[22,23] Bratton[23] reported that the spinel powder from a hydroxide precursor only densified to ~96% of the theoretical density after holding at 1600°C for 6 h.

Sinterability of a wet-chemically derived oxide powder has close relationship with the properties of its precursor. In practice, some carbonates,[24–26] obtained via precipitation using ammonium bicarbonate or sodium carbonate as the precipitant, proved superior to hydroxides as precursors for well-sinterable oxide powders. In these cases, the carbonate precursors were composed of ultrafine crystallites that loosely flocked together to form secondary agglomerates, and the resultant oxide powders showed good dispersion and excellent sinterability. Translucent materials were obtained by vacuum sintering at relatively low temperatures without or with only a small amount of sintering aids. Hokazono et al.[9] once reported a homogeneous precipitation process achieved by the forced hydrolysis of urea at 90°C for the production of Mg–Al spinel powders from a mixed solution of magnesium and aluminum nitrates, which can be viewed as the first attempt to synthesize spinel powders using a carbonate-anions containing solution as the precipitant. However, possibly due to the extremely slow decomposition of urea and the decreased solubility of H_2CO_3 at elevated temperatures, the resultant precursor nearly contained no carbonate anions, and was only a mixture of gel-like amorphous alumina hydrate and $Mg_4Al_2(OH)_{14}{\cdot}3H_2O$ phases. The spinel powder from this precursor was reported to reach 99% of the theoretical density by sintering at 1600°C for 4 h.

In this paper, we have used ammonium bicarbonate as the precipitant to synthesize spinel precursors from a mixed solution of magnesium and aluminum nitrates. Here, we describe the preparation and characterization of the spinel powder, as well as its sintering behavior.

2. Experimental procedure

2.1. Starting materials

Aluminum nitrate nonahydrate (>99% purity), magnesium nitrate hexahydrate (>99% purity), ammonium bicarbonate (ultrahigh purity) and ammonia water (28%, analytical grade) were used as starting materials (all purchased from Kanto Chemical Co., Inc., Tokyo, Japan). As provided by the manufacturer, major cation impurities in the aluminum and magnesium nitrates were sodium (<0.01 wt.%) and calcium (<0.01 wt.%), respectively. All these chemicals were used as received without further purification.

2.2. Powder preparation

The stock solution of salts for spinel synthesis was made by dissolving magnesium and aluminum nitrates into distilled water. To ensure that Mg^{2+} and Al^{3+} would be mixed at the spinel stoichiometry of 1:2 molar ratio, cation contents of the mixed solution were assayed by the ICP (Inductively Coupled Plasma) spectrophotometric technique and were further adjusted. Final concentration of the mixed salt solution was 0.15 M (for Al^{3+}).

Concentration of the precipitant solution was expected to affect composition of the resultant precipitate. Previous work[27] on precipitation of aluminum compounds using ammonium bicarbonate as the precipitant revealed that Al^{3+} cations may precipitate as pseudoboehmite (AlOOH) or ammonium dawsonite [$NH_4Al(OH)_2CO_3$], mainly depending upon the concentration of the precipitant solution and the reaction temperature.

To avoid the possible formation of gelatinous AlOOH, which was expected to cause hard agglomeration, the concentration of the ammonium bicarbonate solution was selected as 1.5 M and the reaction temperature was chosen as 50°C. The initial pH value of the ammonium bicarbonate solution was adjusted to 11.5 with ammonia water, considering that magnesium compounds (such as hydroxide, normal carbonate or basic carbonate) usually have relatively large solubility products and a highly alkaline condition favors their complete precipitation.

The spinel precursor was made by adding 400 ml of the mixed salt solution at a speed of 5 ml/min into 600 ml of the ammonium bicarbonate solution under mild stirring with a subsequent aging period of 24 h at the reaction temperature (50°C). After aging, the suspension has a final pH value of 11.07. The resultant suspension was filtered using suction filtration, washed four times with distilled water (pH adjusted with ammonia water to 11.07), rinsed with ethanol, and dried at room temperature with flowing nitrogen gas over 24 h. The dried cake was lightly crushed with a zirconia pestle and mortar and calcined at various temperatures for 2 h under flowing oxygen (100 ml/min). Unlike gelatinous hydroxide precipitates, the precursor was loosely agglomerated after drying and was quite easy to pulverize with a zirconia pestle and mortar.

2.3. Powder characterization

Differential thermal analysis/thermogravimetry analysis (DTA/TG) of the precursor was performed using a DTA/TG analyzer (Model EXSTAR 6000, Rigaku, Tokyo, Japan) in flowing air (200 ml/min). The heating

rate was 10°C/min and the sample weight was 30 mg. The sample pot was platinum with a depth of 5 mm and the reference material was alpha-alumina.

Phase identification was performed via X-ray diffractometry (XRD) (Model PW 1700 diffractometer, Philips Research Laboratories, Eindhoven, The Netherlands), using nickel-filtered CuK_α radiation and a scanning speed of 1.5° 2θ per min. The crystallite size of the spinel powder was calculated from line-broadening of the (311) peak, using the Philips APD 1700 software (APD 1700, Philips Research Laboratories) from Scherrer's equation:

$$D = K\lambda/\left(h_{1/2}\cos\theta\right) \tag{1}$$

where D is the average crystallite size, K is Scherrer constant (0.9×57.3), λ is the wavelength of incident X-rays (0.15405 nm), $h_{1/2}$ is the peak width at half height and θ corresponds to the peak position.

Powder morphology and microstructure of the sintered body were observed via scanning electron microscopy (SEM) (Model S-5000, Hitachi, Tokyo, Japan). For powders, the sample was ultrasonically dispersed into acetone, and the resultant suspension was spread on the surface of a silicon plate. For sintered bodies, the surface was polished successively to 1 μm finish with diamond paste and thermally etched at 1300°C for 1 h in air to reveal grain boundaries. All samples were coated with a thin layer of carbon for conductivity before observation.

2.4. Compaction and sintering

Two kinds of sintering methods, constant-rate-of-heating (CRH) sintering and vacuum sintering, were used to investigate densification behavior of the spinel powders. For CRH sintering, powders were first dry-pressed manually (~10 MPa pressure) into small cylinders with a diameter of 6 mm and a length of 4–6 mm in a tungsten carbide die and then isostatically compacted at a pressure of 200 MPa. CRH sintering was conducted in air using a thermal mechanical analyzer (TMA, Model 1700, Rigaku, Tokyo, Japan) up to 1550°C at a heating rate of 8°C/min and a cooling rate of 15°C/min. The sintered density, ρ, at any temperature, was determined from the green density ρ_0 and the measured linear shrinkage $\Delta L/L_0$ using the equation:

$$\rho = \rho_0/(1 - \Delta L/L_0)^3 \tag{2}$$

where L_0 is the initial sample length and $\Delta L = L_0 - L$, where L is the instantaneous sample length. The green density of a powder compact was calculated from its weight and geometric dimensions. Relative sintered density was obtained by taking the theoretical density of stoichiometric spinel as 3.58 g/cm^3.[5]

Vacuum sintering was performed in a furnace heated by a tungsten-mesh heater (Model M60-3X8-WW-23, Nemus, Tokyo, Japan). In this case, pellets with dimensions of 12 mm in diameter and 2 mm in thickness were prepared in a double-action tungsten die at about 30 MPa pressure and then isostatically compacted at 200 MPa. During vacuum sintering, the samples were heated at a rate of 8°C/min to selected temperatures and cooled down to room temperature at 15°C/min after holding 2 h at the sintering temperature. The vacuum in the furnace was better than 10^{-3} Pa during residence. Densities of the sintered bodies were determined by Archimedes method with distilled water as the immersion medium.

3. Results and discussion

3.1. Composition and phase evolution of the precursor

Composition of the precursor depends on the supporting anions present and the solubilities of metal cations in solution. This is especially true for the present work, since equilibrium between the precipitate and metal cations in solution was well established during adequate aging. The following chemical reactions were expected in the precipitant solution:

$$H_2O \Longleftrightarrow H^+ + OH^- \tag{3}$$

$$NH_4OH \Longleftrightarrow NH_4^+ + OH^- \tag{4}$$

$$NH_4HCO_3 \Longleftrightarrow NH_4^+ + HCO_3^- \tag{5}$$

$$HCO_3^- \Longleftrightarrow H^+ + CO_3^= \tag{6}$$

$$H^+ + HCO_3^- \Longleftrightarrow H_2CO_3 \tag{7}$$

Therefore, composition of the precursor will be the result of competition between OH^- and carbonate anions during combining with metal cations, and the final composition should assure that Al^{3+} and Mg^{2+} cations have the lowest solubilities in solution under the present precipitation conditions.

Chemical analysis by the chelate-titrimetric method[28] revealed that the precursor contained 14.9 wt.% of Al and 6.7 wt.% Mg. The precursor was stoichiometric within the accuracy of this analysis method (±0.1 wt.%).

Fig. 1 shows XRD spectra of the precursor and its calcination products. The as-synthesized precursor (Fig. 1a) was crystalline and was identified as a mixture of ammonium dawsonite hydrate [$NH_4Al(OH)_2CO_3{\cdot}H_2O$]

(JCPDS Card No. 29-106) and hydrotalcite [$Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$] (JCPDS Card No. 22-700) phases. A foregoing experiment using individual solutions of aluminum and magnesium nitrates yielded crystalline ammonium dawsonite hydrate and ammonium magnesium carbonate hydrate [$(NH_4)_2Mg(CO_3)_2{\cdot}4H_2O$] (JCPDS Card No. 33-66), respectively, under precipitation conditions similar to those used for spinel synthesis. This phenomena indicates that hydrotalcite has a quite low solubility product, and its formation can further decrease the solubilities of Al^{3+} and Mg^{2+} cations in solution. Hydrotalcite belongs to a group of layered Mg/Al double hydroxides[29] with a structure derived from brucite [$Mg(OH)_2$] where trivalent aluminum cations replace some of the divalent magnesium cations, which creates a net positive charge on the layers. The overall electro-neutrality is obtained by the intercalation of $CO_3^{=}$ anions into the interlayer spaces, coexisting with crystal water. Many Mg/Al double hydroxides, such as $Mg_2Al(OH)_7$[7,8,11] and $Mg_4Al_2(OH)_{14}{\cdot}3H_2O$,[9,12] were frequent products during spinel synthesis by sol–gel of metal alkoxides or coprecipitation from inorganic salts. The importance of the formation of Mg/Al double hydroxides is that spinel is a direct decomposition product during heat treatment.

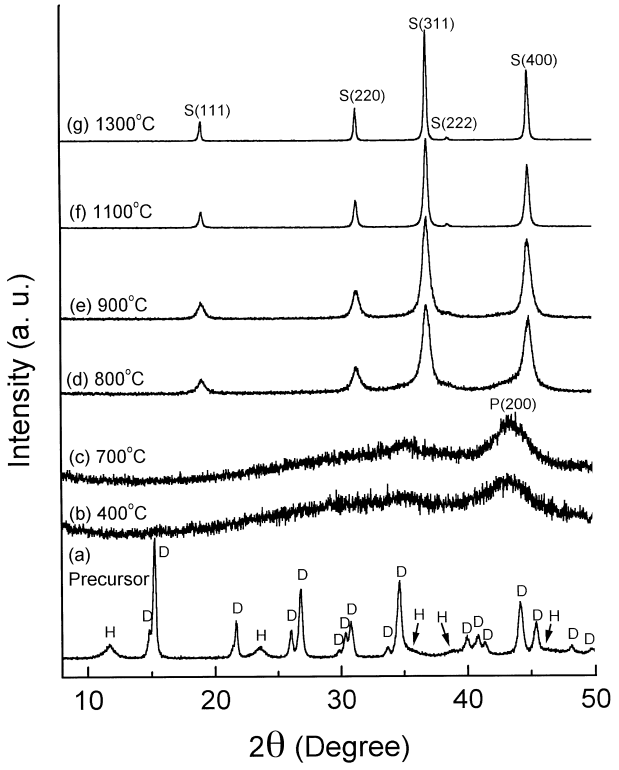

Fig. 1. XRD spectra of the precursor and the calcined powders. H: hydrotalcite [$Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$], D: ammonium dawsonite hydrate [$NH_4Al(OH)_2CO_3{\cdot}H_2O$], P: periclase (MgO) and S: spinel ($MgAl_2O_4$).

XRD patterns of the calcined powders were shown in Fig. 1(b)–(g). Calcination products of the precursor were essentially amorphous to X-rays in the temperature range of 200–400°C. Between 400 and 700°C, broad peaks corresponding to periclase (MgO) (JCPDS Card No. 45-946), decomposed from the hydrotalcite, appeared in the XRD patterns. Previous work[7,8,12] demonstrated that some Mg/Al double hydroxides, such as $Mg_2Al(OH)_7$ and $Mg_4Al_2(OH)_{14}{\cdot}3H_2O$, decomposed to crystalline spinel and periclase at temperatures as low as 400–500°C. In our case, however, crystalline spinel was not observed up to 700°C, which may indicate that complete dissolution of MgO from the hydrotalcite has not yet been achieved. This is reasonable considering that the hydrotalcite possesses a higher Mg/Al molar ratio when compared with $Mg_2Al(OH)_7$ $Mg_4Al_2(OH)_{14}{\cdot}3H_2O$.

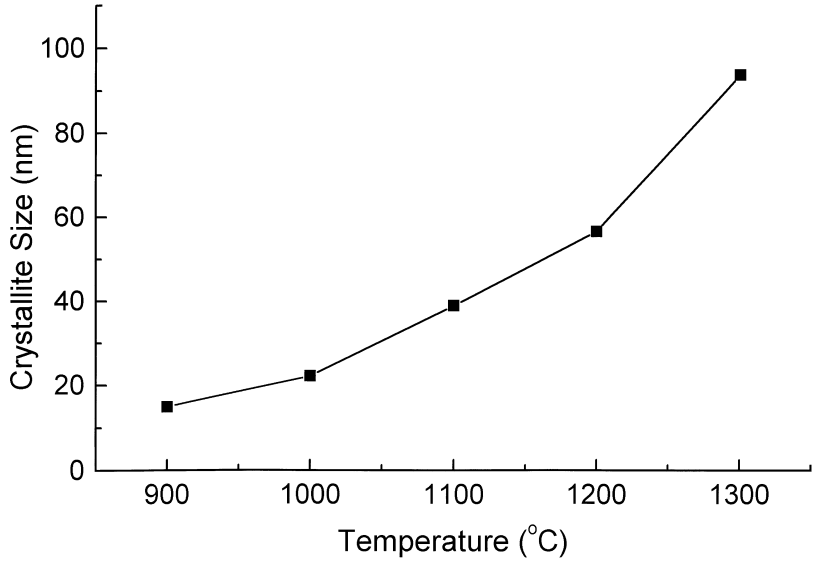

Fig. 2. Crystallite size of the spinel powder, as a function of the calcination temperature.

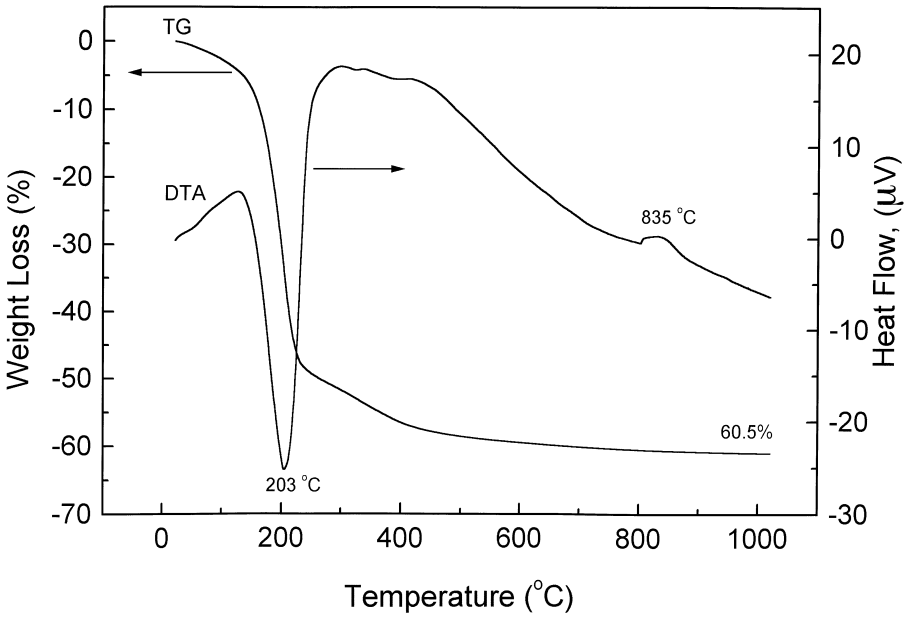

Fig. 3. DTA/TG curves of the precursor.

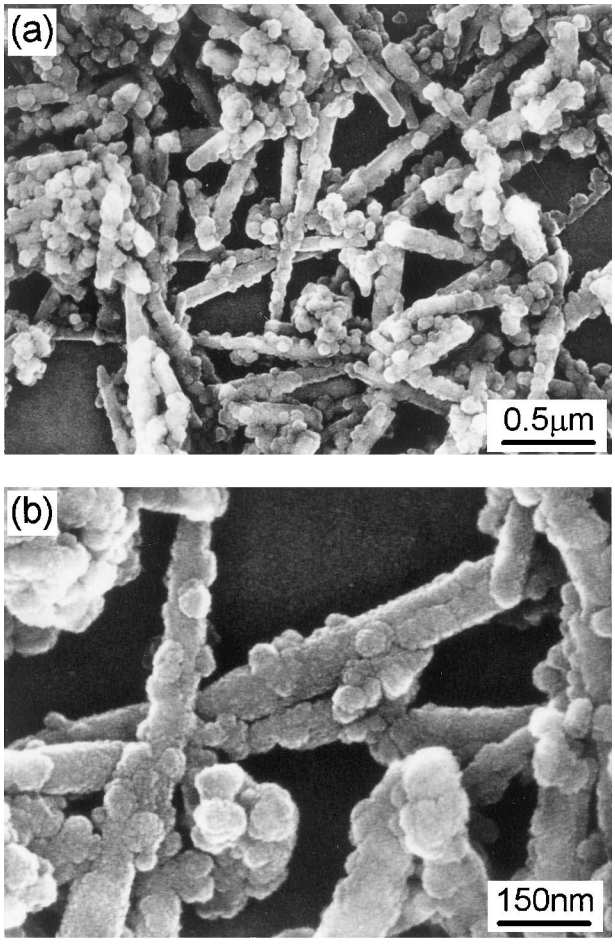

Fig. 4. SEM micrographs showing morphology of the precursor (a) observed under low magnification and (b) observed under high magnification.

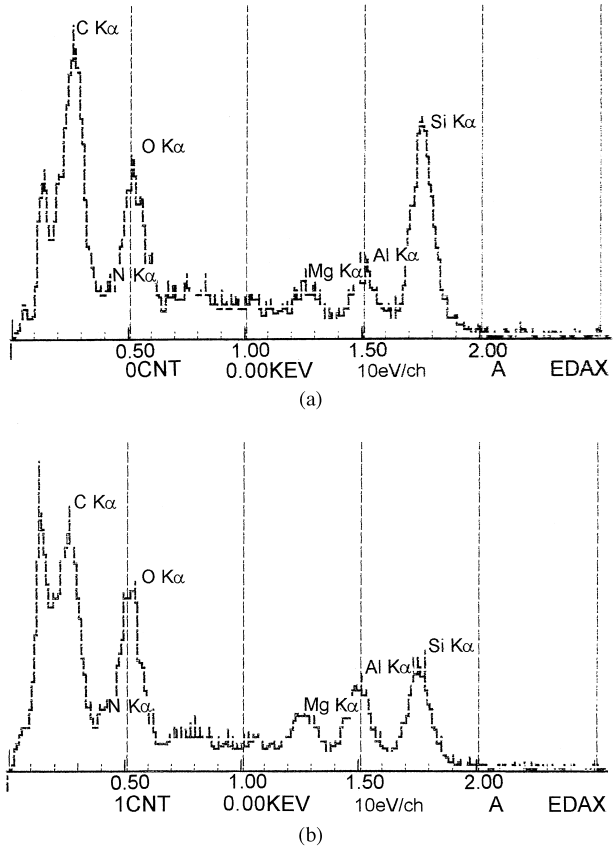

Fig. 5. The results of qualitative EDX analysis performed on (a) spherical particles and (b) rodlike particles in the precursor.

Mass formation of $MgAl_2O_4$ spinel (JCPDS Card No. 21-1152) mainly occurred at ~800°C through solid-state reaction between periclase and a polymorph of alumina, most likely γ-Al_2O_3,[30] decomposed from the ammonium dawsonite hydrate. The γ-Al_2O_3 derived from ammonium dawsonite was known to be ultrafine (< 5 nm) and highly reactive,[30] while the MgO decomposed from hydrotalcite may also possess high reactivity since its crystallite size at 700°C is only ~3 nm, as determined by the XRD line-broadening technique performed on the (200) peak. Due to the high reactivity of γ-Al_2O_3 and MgO as well as their intimate mixing, complete conversion of the precursor to spinel was almost achieved at a relatively low calcination temperature of 900°C (Fig. 1e), though solid-state reaction was required. Above 900°C, continued refinement in peak shapes and intensities, mainly caused by crystallite growth, were observed along with an increase in the calcination temperature.

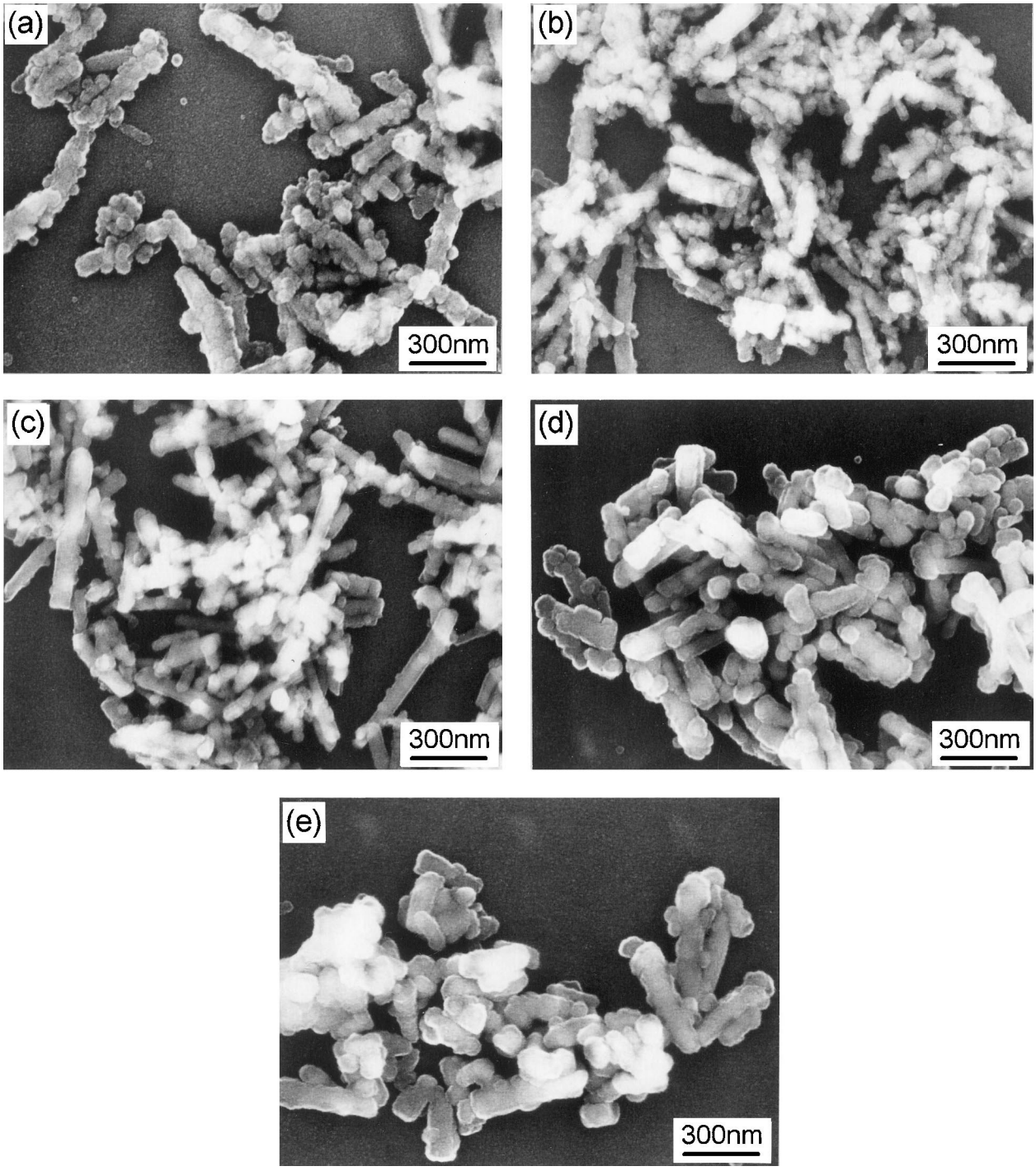

Fig. 6. SEM micrographs showing morphology of the spinel powder calcined at (a) 900, (b) 1000, (c) 1100, (d) 1200 and (e) 1300°C.

In Fig. 1, one may notice that the γ-Al_2O_3 phase was not clearly detected with XRD at 800°C. There are two main possibilities. One is that the Mg–Al spinel and γ-Al_2O_3 (JCPDS Card No. 10-425) have the same cubic crystal structure, and the XRD patterns of these two phases are very similar and the major peaks merge. For example, the most intense peak ($I=100\%$) for the spinel is the (311) reflection with a d-spacing of 0.2437 nm, while that for γ-Al_2O_3 is the (400) reflection with a similar d-spacing of 0.1977 nm. Besides, γ-Al_2O_3 usually shows poor crystallinity,[30] and its amount at 800°C became small due to the consumption by spinel formation. These made the clear detection of γ-Al_2O_3 phase difficult, even if it exists as an individual phase. The second possibility is that γ-Al_2O_3 was in the form of solid solution. A continuous solid solution exists from spinel and γ-Al_2O_3. For the Al_2O_3–MgO system, a stabilized γ-Al_2O_3–$MgAl_2O_4$ solid solution may form before crystallization of a pure spinel phase during heat treatment, and its formation is in competition with that of the spinel phase. Several methods have been suggested to determine whether the solid-solution was formed or not. One method, proposed by Yoo et al.,[31] is measuring the lattice parameter a of the cubic cell of the spinel or the position of the XRD lines on the 2θ scale. In this way, the composition of the solid solution can be deduced since the composition dependence of the a value satisfies Vegard's law. Another simple method, suggested by Pasquir et al.,[14] concerns the comparison of the relative intensities of the (400) and (311) peaks. A pure stoichiometric spinel should have $X=I_{(400)}/I_{(311)}=0.6$ (more accurately, $X=0.65$, according to JCPDS Card No. 21-1152), while $X>0.65$ indicates a solid solution of γ-Al_2O_3 and spinel. According to Fig. 1 of the present work, the X value at 800°C is 0.87, indicating that γ-Al_2O_3, at least partially, was in the form of solid solution. Increasing the calcination temperature decreased the X value gradually, and the X value at 1300°C is 0.64, very close to that of the stoichiometric spinel.

Fig. 2 gives the approximate crystallite size of the spinel powder, as a function of the calcination temperature. Ultrafine spinel powders were produced by calcining the precursor at temperatures below 1300°C. The spinel powders produced at 900 and 1300°C have crystallite sizes of ~15 and ~94 nm, respectively, as determined by the XRD line-broadening technique.

DTA/TG curves (Fig. 3) of the precursor revealed three major thermal events and a total weight loss of ~60.5% up to 1000°C. This weight loss is quite close to the theoretical mass loss (60.73%) calculated for a stoichiometric mixture of $NH_4Al(OH)_2CO_3{\cdot}H_2O$ and $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$. The huge and sharp endothermic peak, located at ~203°C, was caused by the decomposition of ammonium dawsonite into AlOOH[27,30] and the release of crystal water and CO_2 from hydrotalcite. The calculated weight loss (50.7%) for this thermal event agrees well with that revealed by the TG curve at 300°C (~51.5%). The double-shouldered shallow endothermic peak, located between ~300–450°C, corresponds to the dehydroxylation of the hydroxide mixture into oxides. The successive small weight loss at even higher temperatures (>450°C) may be caused by further dehydration. In accordance with Fig. 1d, the exothermic peak centered at ~835°C was assigned to the mass formation of spinel, though the thermal effect due to lattice ordering of the spinel decomposed from hydrotalcite could not be completely excluded. The

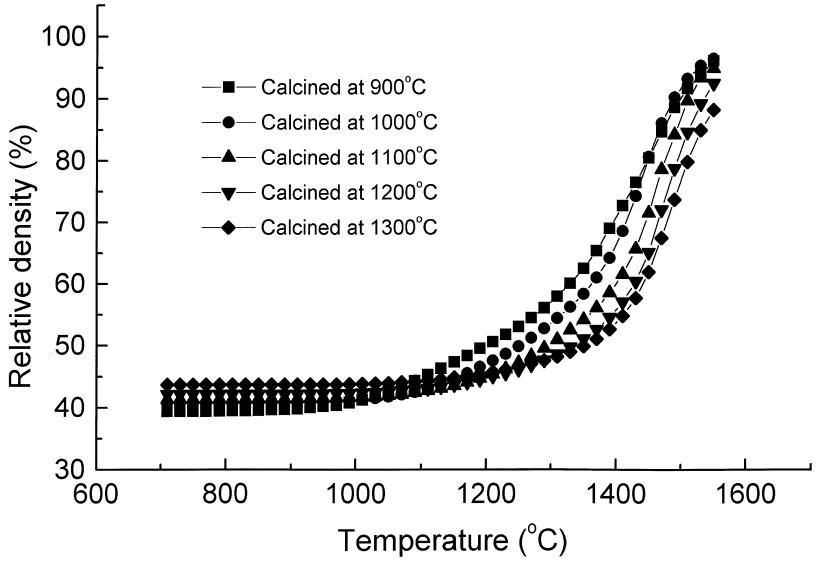

Fig. 7. Relative density versus temperature for spinel powders under CRH sintering at a heating rate of 8°C/min.

broad feature of the exothermic peak may also indicate that the spinel phase was formed mainly via solid-state reaction. A similar exothermic event caused by spinel formation was also observed by Montouillout et al.[16] for a spray dried precursor which was believed to be diphasic.

3.2. Powder morphology

Fig. 4 shows particle morphology of the precursor. Low-magnification (Fig. 4a) revealed that the precursor contained two kinds of particles: rodlike particles (~0.08–0.14 μm in diameter and ~0.3–1.5 μm in length) and relatively spherical particles (~70–100 nm in diameter). Higher magnification (Fig. 4b) showed that both the rods and the spheres are composed of extremely fine particles and are essentially secondary agglomerates of primary particles. Qualitative EDX analysis has been performed on both the rods and the spheres in the precursor, and the results were given in Fig. 5(a) and (b), respectively. It should be noted that, in each case, the first peak from the left side could not match any element and was caused by noise, while the silicon peak was attributed to the silicon plate used as a supporting substrate. The extraordinary strong carbon peak was mainly due to the carbon film coated on particle surfaces, though the particles themselves also contain carbon element. From Fig. 5, one may notice that both the rods and the spheres contained magnesium and aluminum elements, indicating that the precursor possessed high cation homogeneity.

Fig. 6 showed morphologies of the spinel powders calcined at selected temperatures. The pseudomorphs of the precursor retained to the spinel powders calcined in the temperature ranges of 900–1100°C, though appreciable reduction in the amount and the length of the rodlike particles were observed [Fig. 6(a)–(c)]. Calcination at temperatures of $\geqslant$ 1200°C caused a drastic change in the particle morphology [Figs. 6(d)–(e)]:the rodlike particles nearly completely collapsed into rounded particles and were only occasionally observed.

3.3. Sintering behavior of the spinel powders

Fig. 7 shows the results of CRH sintering. Due to crystallite growth and loss in reactivity, the spinel powder calcined at a higher temperature showed a higher onset temperature of rapid densification. The powders calcined in the temperature range of 900–1200°C showed good sinterability and densified to their respective relative densities of ~96.0, ~96.4, ~94.8 and ~92.4% up to 1550°C at a constant heating rate of 8°C/min. While that calcined at 1300°C only sintered to ~88.2% of the theoretical density.

Fig. 8 shows microstructures of the sintered bodies after TMA measurement using powders calcined at 1000–1200°C. Micron-sized large pores were observed in all the sintered bodies. Considering that these pores have a size comparable to the average grain size (~1.9 μm), they will be difficult to eliminate by the normal sintering mechanisms (grain-boundary diffusion or lattice diffusion) and are removable through abnormal

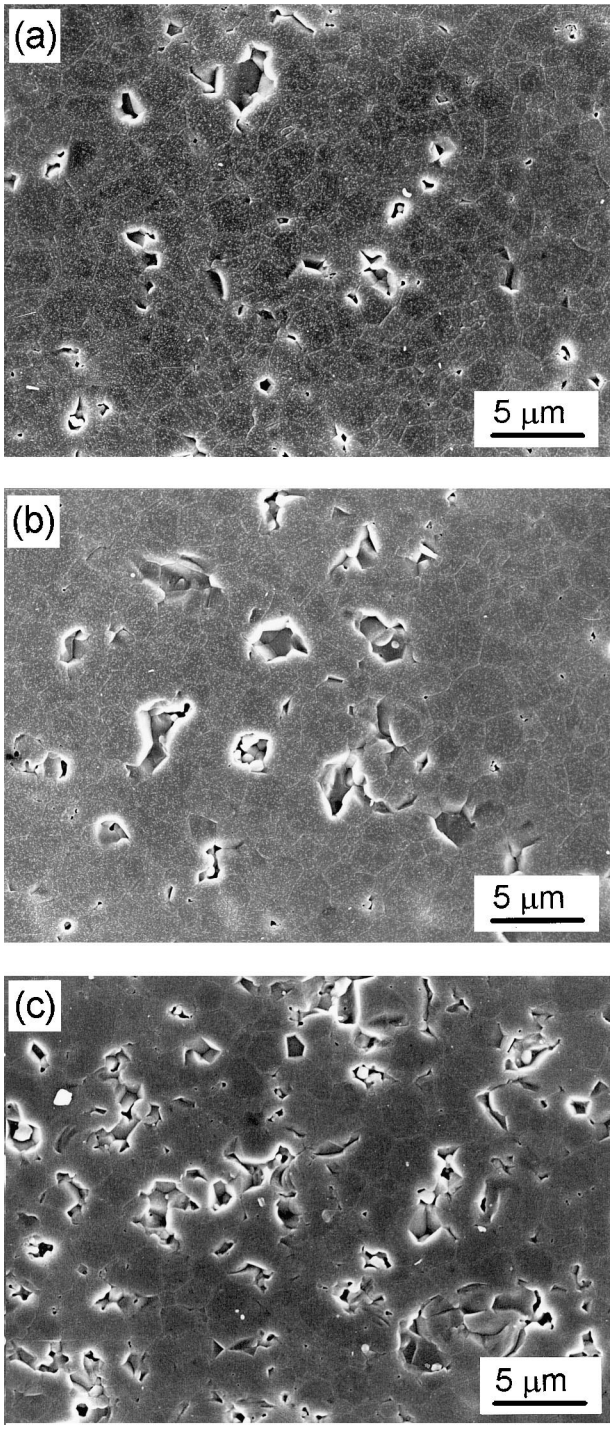

Fig. 8. SEM micrographs showing microstructures of the spinel ceramics sintered under CRH conditions using powders calcined (a) 1000, (b) 1100 and (c) 1200°C.

grain growth during further densification.[32,33] The origin of these large defects in the sintered materials may be explained from the view point of the compaction homogeneity of particles in the green bodies. As shown in Fig. 6(a)–(c), the spinel powders produced at or below 1100°C contained a considerable amount of rodlike particles, which made homogeneous compaction nearly impossible. While the powders calcined at higher temperatures (1200–1300°C) contained an increased amount of hard aggregates, which was clearly felt during powder processing, though the individual particle possessed a more suitable morphology [Fig. 6(d)–(e)] for uniform compaction.

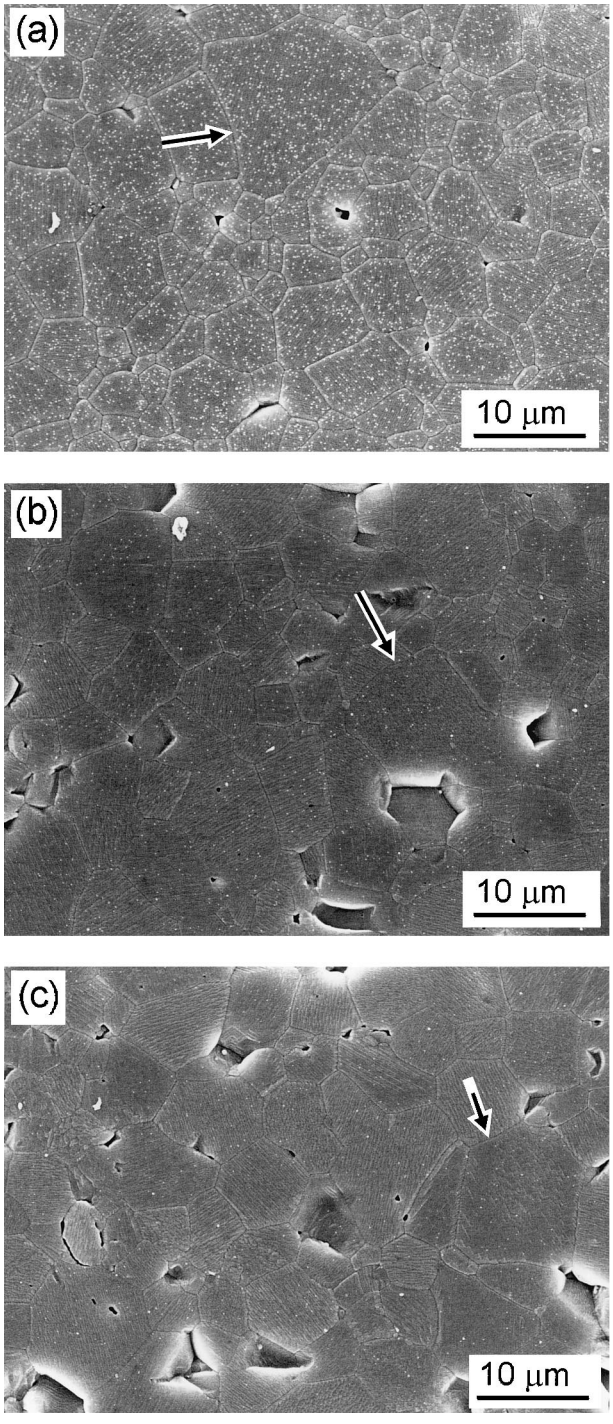

Fig. 9. SEM micrographs showing microstructures of spinel ceramics sintered under vacuum at 1550°C for 2 h using powders calcined at (a) 1000, (b) 1100 and (c) 1200°C. Some abnormally grown grains were indicated by arrows.

Fig. 9 showed microstructures of the spinel ceramics fired under vacuum at 1550°C for 2 h, using the powders calcined at 1000–1200°C. The relative sintered densities, as determined by Archimedes method, were ~98.5, ~97.8 and ~97.2% for the powders calcined at 1000, 1100 and 1200°C, respectively. All the sintered bodies have a mean grain size of ~5.0 μm. Exaggerated grain growth were observed for all the powders during densification, as indicated by arrows in Fig. 9(a)–(c). To improve the densification behavior of the spinel powders and hence properties of the sintered materials, future studies will be aimed at avoiding the formation of rodlike particles during precipitation or enhancing the collapse of rodlike particles in the temperature range of 900–1100°C to obtain a suitable powder that will take full advantages of the present method, i.e. the low formation temperature of spinel phase and the ultrafine nature of the resultant spinel powders.

4. Conclusions

A precursor for $MgAl_2O_4$ spinel was synthesized via precipitation, using ammonium bicarbonate as the precipitant. The precursor was composed of crystalline ammonium dawsonite hydrate [$NH_4Al(OH)_2CO_3 \cdot H_2O$] and hydrotalcite [$Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$] phases. The spinel phase formed by the decomposition of hydrotalcite at lower temperatures (400–800°C) and a solid-state reaction between MgO (decomposed from hydrotalcite) and γ-Al_2O_3 (derived from ammonium dawsonite hydrate) at higher temperatures (>800°C). The spinel powders calcined at below 1300°C are ultrafine grained, i.e. less than 100 nm. Spinel ceramics of ~98.5% dense were obtained at 1550°C for 2 h under vacuum, using the powders calcined at 1000°C. Due to the non-uniform compaction of particles, caused by undesirable particle morphology and aggregates, abnormal grain growth occurred during densification. Further studies will be aimed at producing a more homogeneous spinel powder that will take full advantage of the fine crystallite size.

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