ELSEVIER

Ceramics International 27 (2001) 481–489

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# A wet-chemical process yielding reactive magnesium aluminate spinel ($MgAl_2O_4$) powder

Ji-Guang Li *, Takayasu Ikegami, Jong-Heun Lee, Toshiyuki Mori, Yoshiyuki Yajima

*National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan*

Received 18 April 2000; received in revised form 22 June 2000; accepted 2 October 2000

## Abstract

Ammonium carbonate was used as the precipitant to synthesize Mg–Al spinel precursors from a mixed solution of magnesium and aluminum nitrates. The precursor, 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, transformed to pure spinel at ~900°C via the decomposition of hydrotalcite at ~400–800°C and a solid-state reaction between MgO (decomposed from hydrotalcite) and $\gamma$-$Al_2O_3$ (derived from $NH_4Al(OH)_2CO_3{\cdot}H_2O$) at ~800–900°C. Sinterability of the resultant spinel powders was evaluated by the constant-rate-of-heating sintering method. The effect of calcination temperature on particle morphology and sinterability of the resultant spinel powders was investigated. Spinel ceramics of ~99% dense were produced by vacuum sintering at 1550°C for 2 h from the powder calcined at 1100°C for 2 h. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* A. Sintering; Mg–Al spinel; Chemical synthesis; Ammonium carbonate

## 1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) possesses a unique combination of desirable properties: 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 be widely used in diverse engineering fields. However, dense materials 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, since the volume expansion (5%) accompanying the spinellization reaction [6] is detrimental to densification. 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.

The successful fabrication of dense spinels at reasonable firing temperatures seems to lie in the production of highly reactive, phase-pure spinel powders. In recent years, various wet-chemical techniques or wet-chemical assisted techniques, such as 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], have been developed and successfully used for the production of pure spinel powders. In general, the spinel powders prepared by these methods showed a higher degree of chemical homogeneity, better control of stoichiometry and improved sinterability, when compared with those synthesized by the conventional solid-state reaction method. Among the above wet-chemical processes, precipitation using inorganic salts should be a relatively convenient and cost-effective way. But mainly due to severe agglomeration, the spinel powder produced by hydroxide coprecipitation using ammonia water as precipitant has not been sinterable enough to achieve full densification via pressureless sintering without additives [22,23]. Bratton [23] reported that the spinel powder derived from a hydroxide precursor only sintered to 96% of the theoretical density at 1600°C for 6 h.

---

* Corresponding author. Tel.: +81-0298-51-3354, Ext. 2247; fax: +81-0298-52-7449.

*E-mail address:* jgli@nirim.go.jp (J.-G. Li).

PII: S0272-8842(00)00107-3

Sinterability of a wet-chemically derived oxide powder has close relationship with the properties of its precursor. In practice, some carbonates [24–26] with controlled chemical composition and particle morphology, obtained via precipitation using ammonium bicarbonate or sodium carbonate as the precipitant, proved superior to hydroxides as precursors for less-agglomerated oxide powders. In these cases, the oxide powders showed excellent sinterability, and 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. This work 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 1600C for 4 h. To our best knowledge, there has been no report concerning the use of ammonium carbonate as a precipitant for the production of spinel powders via precipitation.

In this paper, we have used ammonium carbonate to synthesize spinel precursors from a mixed solution of magnesium and aluminum nitrates. Ultrafine spinel powders ($<100$ nm) were obtained by calcining the precursor in the temperature range of 900–1200°C. Here, we describe the preparation and characterization of the spinel powder, as well as its densification behavior.

## 2. Experimental procedure

Aluminum nitrate nonahydrate ($>99\%$ purity), magnesium nitrate hexahydrate ($>99\%$ purity), ammonium carbonate (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.

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) spectroscopic technique and were further adjusted. Final concentration of the mixed salt solution was 0.15 mol/dm$^3$ (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 precipitant revealed that $Al^{3+}$ cations may precipitate as pseudoboehmite (AlOOH) or ammonium dawsonite [$NH_4Al(OH)_2CO_3$], mainly depending on 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 ammonium carbonate solution was selected as 1.5 mol/dm$^3$ and the reaction temperature was chosen as 50°C. The initial pH value of the ammonium carbonate 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 carbonate 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 11.21. The resultant suspension was filtered using suction filtration, washed four times with distilled water (pH adjusted with ammonia water to 11.21), 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). The precursor was loosely agglomerated after drying and was quite easy to pulverize with a zirconia pestle and mortar.

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 Cu-$K_\alpha$ radiation and a scanning speed of 1.5° $2\theta$/min. The crystallite size of the spinel powders was calculated from line-broadening of the (311) peak, using the Philips APD 1700 soft ware (APD 1700, Philips Research Laboratories) from the Scherrer equation:

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

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

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, $\rho$, at any temperature, was determined from the green density $\rho_0$ and the measured linear shrinkage $\Delta L/L_0$ using the equation:

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

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 ~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 the selected temperatures and cooled down to room temperature at 15°C/min after holding 2 h at the sintering temperatures. 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 intrusion medium.

## 3. Results and discussion

Composition of the precursor depends on the supporting anions present and the solubilities of metal cations in solution. The following chemical reactions were expected in the precipitant solution:

$$H_2O \Longleftrightarrow H^+ + OH^- \quad (3)$$

$$NH_4OH \Longleftrightarrow NH_4^+ + OH^- \quad (4)$$

$$(NH_4)_2CO_3 \Longleftrightarrow 2NH_4^+ + CO_3^= \quad (5)$$

$$H^+ + CO_3^= \Longleftrightarrow HCO_3^- \quad (6)$$

$$H^+ + HCO_3^- \Longleftrightarrow H_2CO_3 \quad (7)$$

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.

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

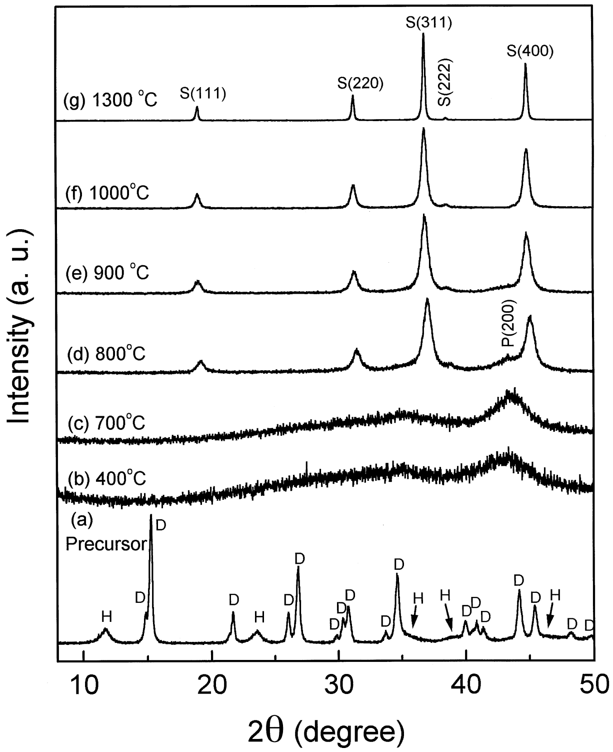


Fig. 1. XRD spectra of the precursor and the calcined powders. H: hydrotalcite [$Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$], D: ammonium dawsonite hydrate [$NH_4Al(OH)_2CO_3\cdot H_2O$], P: periclase (MgO) and S: spinel ($MgAl_2O_4$).

of ammonium dawsonite hydrate [$NH_4Al(OH)_2CO_3H_2O$] (JCPDS Card No. 29-106) and hydrotalcite [$Mg_6Al_2(CO_3)(OH)_{16}4H_2O$] (JCPDS Card No. 22-700) phases. This result is identical to that obtained from the same salt solution when ammonium bicarbonate was used instead of ammonium carbonate as the precipitant [28]. 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. The net positive charges on the layers due to the replacement was compensated by the intercalation of $CO_3^=$ anions into the inter-layer spaces, coexisting with crystal water. Many Mg/Al double hydroxides, such as $Mg_2Al(OH)_7$ [7,8,11] and $Mg_4Al_2(OH)_{14}3H_2O$ [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.

XRD patterns of the calcined powders were shown in Fig. 1b–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 No.45-946), decomposed from 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 $Mg_4Al_2(OH)_{14}3H_2O$, 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 hydrotalcite possesses a higher Mg/Al molar ratio when compared with $Mg_2Al(OH)_7$ or $Mg_4Al_2(OH)_{14}3H_2O$. Mass formation of spinel started at 800°C through solid-state reaction between periclase and a polymorph of alumina decomposed from ammonium dawsonite hydrate. Though not detected with XRD, the alumina polymorph at 800°C is most likely $\gamma$-$Al_2O_3$ [30], which usually shows low crystallinity and transforms to highly crystalline $\alpha$-$Al_2O_3$ via $\theta$-$Al_2O_3$ at ~1200°C [30]. The $\gamma$-$Al_2O_3$ 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 X-ray line-broadening technique performed on the (200) peak. Due to the high reactivity of $\gamma$-$Al_2O_3$ and MgO as well as their intimate mixing, complete conversion of the precursor to spinel (JCPDS Card No. 21-1152) was nearly achieved by calcination at 900°C for 2 h, with only a small amount of periclase detected. Above 900°C, continued refinement in peak shapes and intensities were observed, indicating crystallite growth as the calcination temperature increases.

Fig. 2 gives the crystallite size of the spinel powder, as a function of the calcination temperature. The spinel powders produced at 900 and 1300°C have crystallite sizes of ~15 nm and ~114 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 ~60.3% up to 1000°C. This weight loss is quite close to the theoretical mass loss (60.73%) calculated for a stoichiometric mixture of $NH_4Al(OH)_2CO_3H_2O$ and $Mg_6Al_2(CO_3)(OH)_{16}4H_2O$ phases. The huge and sharp endothermic peak, located at ~225°C, was caused by the decomposition of ammonium dawsonite into AlOOH

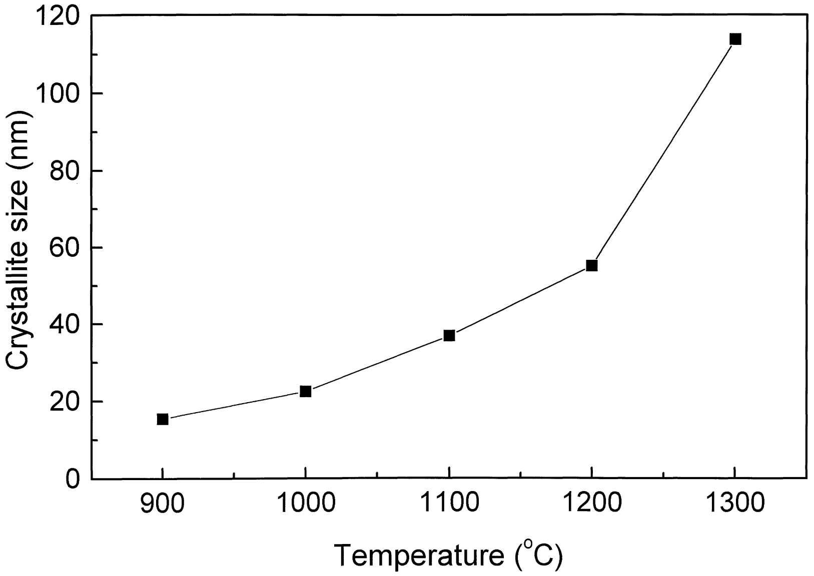


Fig. 2. Crystallite size of the spinel powder, as a function of the calcination temperature.

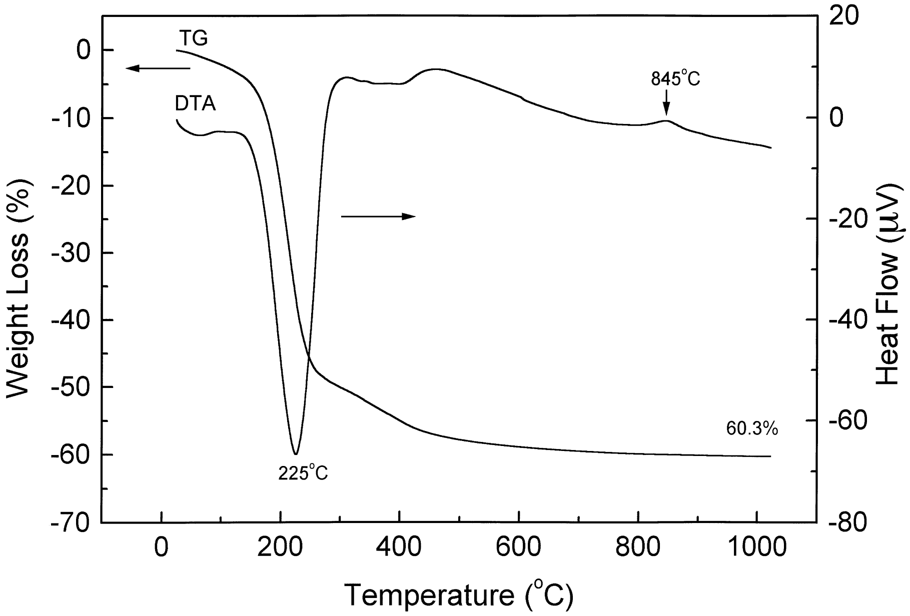


Fig. 3. DTA/TG curves of the precursor.

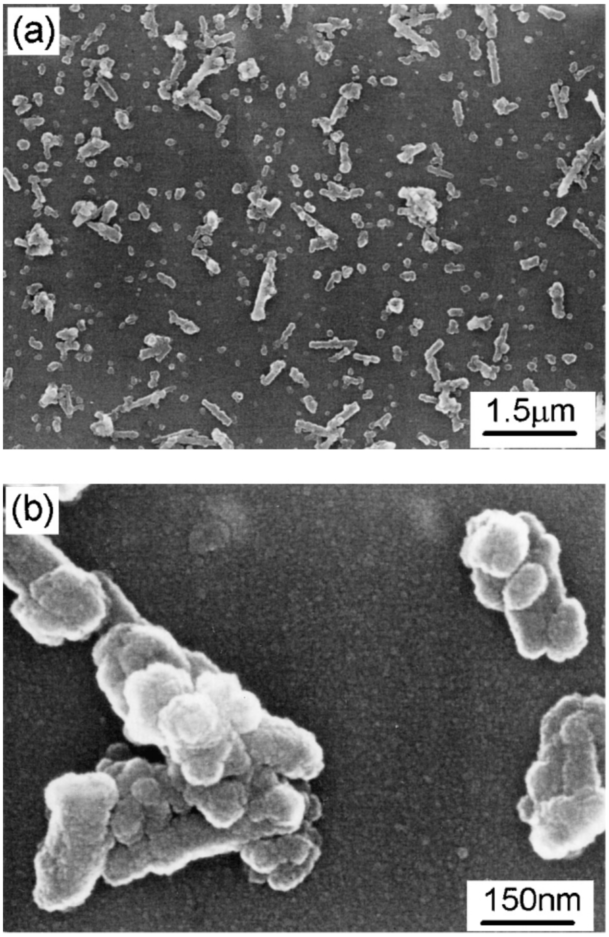
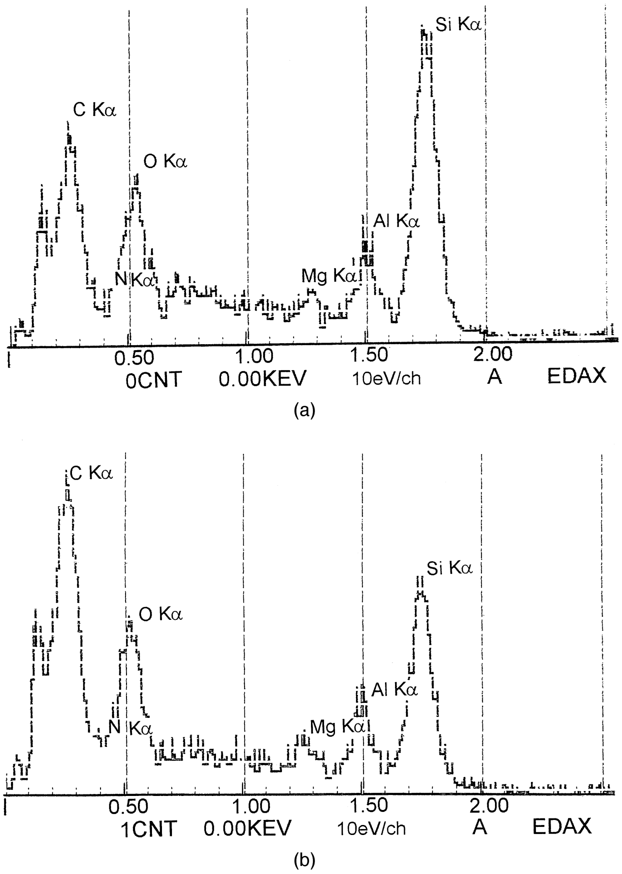


Fig. 4. SEM micrographs showing morphology of the precursor (a) observed under low magnification and (b) observed under high magnification.



(a)

(b)

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

[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 (~50.1%). The decomposition temperature of ammonium dawsonite obtained in the present study agrees well with that (~230°C) reported by Kato et al. [27], while was about 50°C higher than the result (~180°C) obtained by Hayashi et al. [30]. The decomposition temperature of ammonium dawsonite has close relationship with its crystallinity [30]. The broad and shallow endothermic peak, located between ~300 and 450°C, corresponds to the dehydroxylation of the mixed hydroxides 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 broad exothermic peak centered at ~845°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.

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

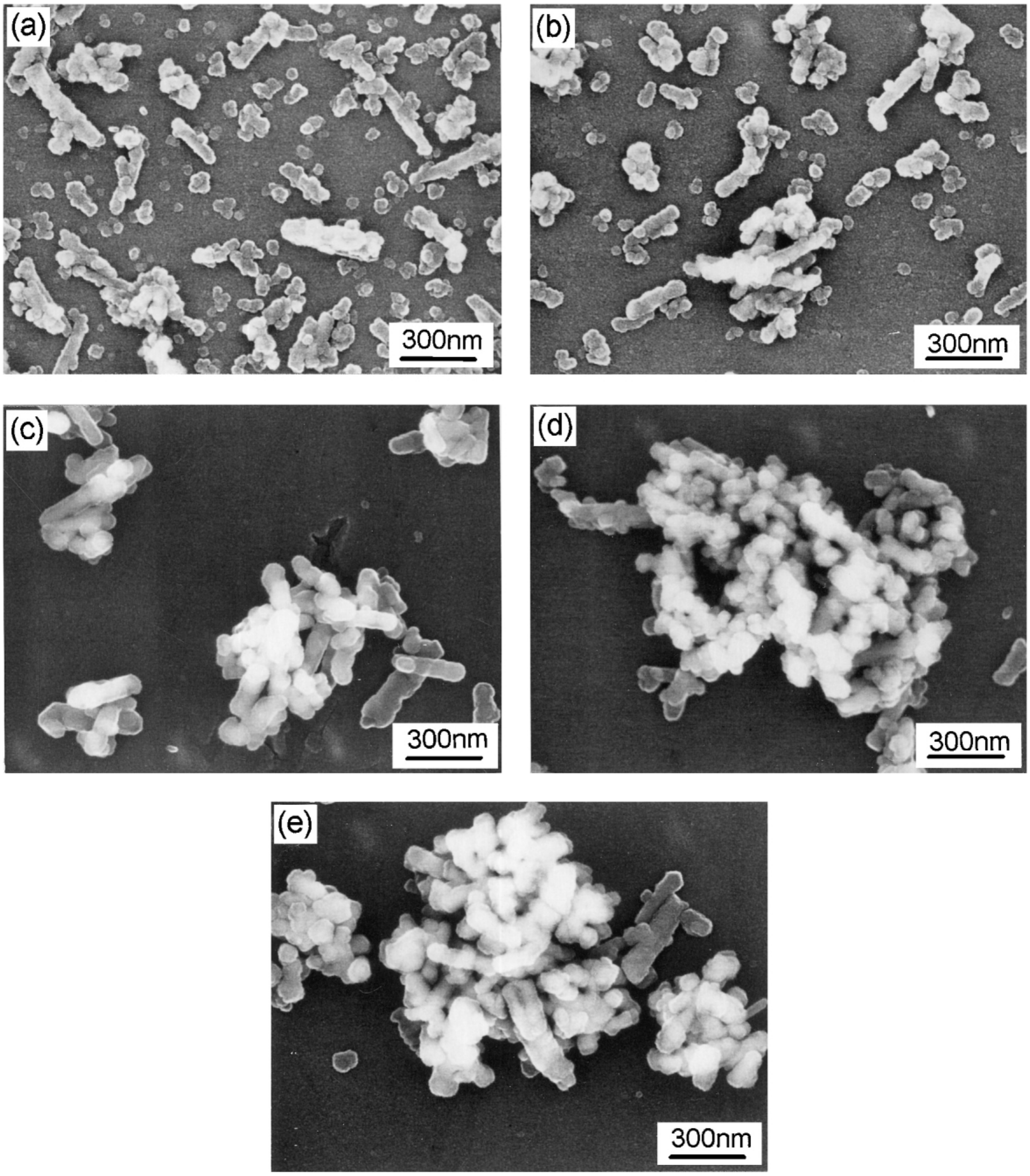


Fig. 6. SEM micrographs showing morphology of the spinel powder calcined at (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C and (e) 1300°C.

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. 5a and b, respectively. Please note 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 a high cation homogeneity.

Fig. 6 showed morphologies of the spinel powders calcined at selected temperatures. The pseudomorphs of the precursor remained in the spinel powders calcined in the temperature ranges of 900–1100°C, though appreciable successive reduction in the amount and the length of the rodlike particles were observed (Fig. 6a–c) with increasing calcination temperature. Calcining the precursor at temperatures of ⩾1200°C caused a drastic change in the particle morphology, and the rodlike particles nearly completely collapsed into rounded particles and were only occasionally visible (Fig. 6d and e).

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 spinel powders produced in the temperature range of 900–1200°C showed good sinterability and densified to their respective relative densities of 95.76, 96.07, 96.77 and 93.01% up to 1550°C at a constant heating rate of 8°C/min. While the powder calcined at 1300°C only sintered to ~83.2% of the theoretical density, showing the poorest sinterability.

Judged from Fig. 7, the most favorable calcination temperature for a reactive spinel powder was 1100°C. The powder produced at this temperature showed the highest densification kinetics in the temperature range of 1300–1550°C and reached the highest final sintered density. Numerous investigations [31–34] revealed that, for a given sintering schedule, the final density of a powder compact mainly depends upon the reactivity (crystallite/particle size) of the powder and the compaction uniformity of particles in the green body. In the present work, the powders calcined at lower temperatures (900–1000°C), though possessed smaller crystallite size and hence higher reactivity (Fig. 3), did not sinter to the highest final densities mainly due to the presence of a relatively large amount of rodlike particles (Fig. 6a and b) which rendered difficulties to uniform compaction. On the other hand, crystallite growth (reactivity loss) (Fig. 2) and the formation of hard aggregates, which was clearly felt during powder processing, were mainly responsible for the decreased final densities of the powders calcined at higher temperatures (1200–1300°C), though the powders possessed a more suitable morphology of individual particles for uniform compaction (Fig. 6c and d). Considering these two aspects, only the spinel powder calcined at 1100°C was used for vacuum sintering.

Fig. 8 shows microstructures of the spinel ceramics fired at selected temperatures for 2 h, using the powder calcined at 1100°C. The materials sintered at 1400, 1475 and 1550°C had relative densities of ~87.9, ~96.1 and ~99.0%, respectively, as determined by Archimedes method. Large (micron sized) pore defects, caused by non-uniform compaction due to the presence of elongated

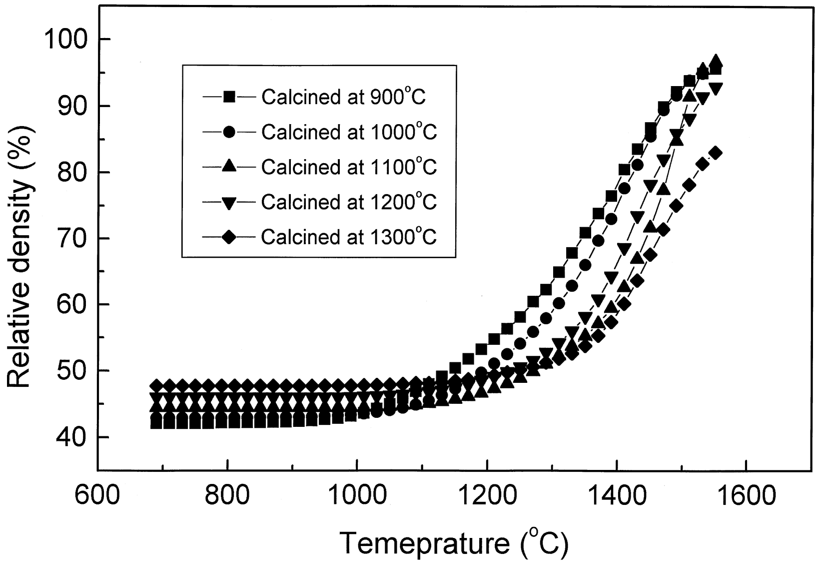


Fig. 7. Relative density versus temperature for spinel powders under CRH sintering at a heating rate of 8°C/min.

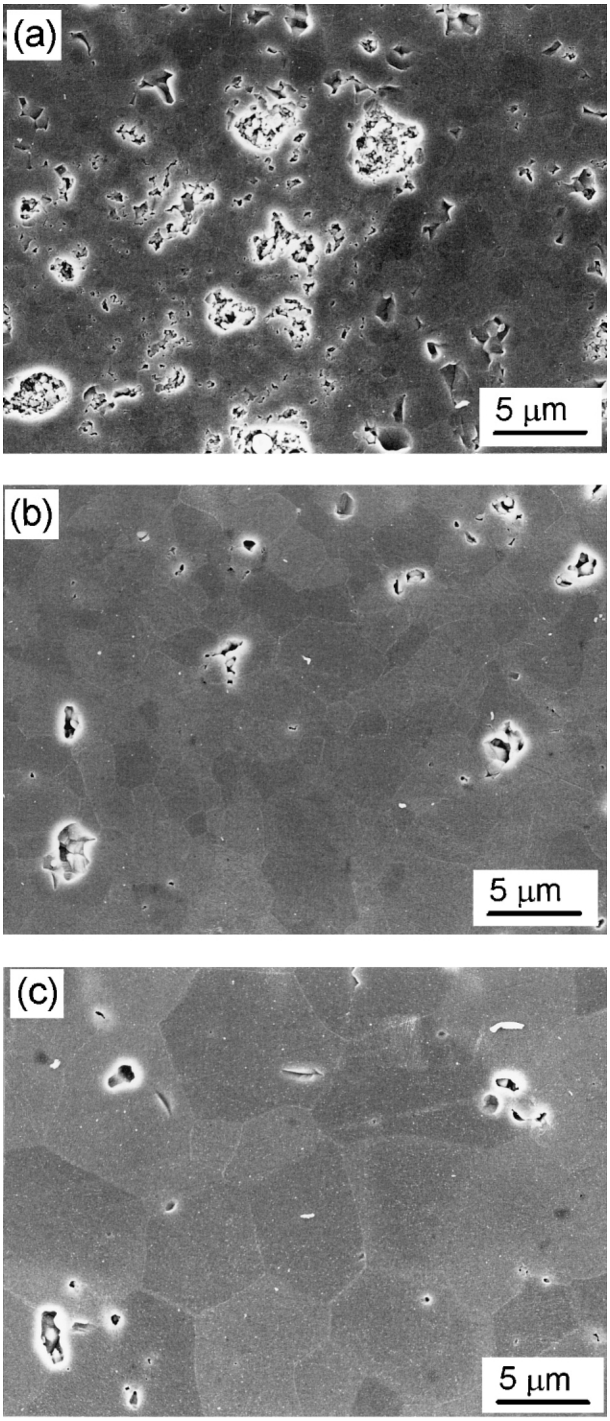


Fig. 8. SEM micrographs showing microstructures of the spinel ceramics sintered at (a) 1400°C, (b) 1475°C and (c) 1550°C for 2 h under vacuum, using the powder calcined at 1100°C for 2 h.

particles and/or aggregates in the starting powder, were clearly observed in the microstructures of all the sintered spinel ceramics. To improve densification behavior of the powder and hence properties of the sintered spinel ceramics, future studies will be aimed at producing a more homogeneous powder with desirable particle morphology that will take full advantages of the present synthesis method, i.e. low formation temperature of the 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 carbonate as the precipitant. The precursor was composed of crystalline ammonium dawsonite hydrate $[NH_4Al(OH)_2CO_3H_2O]$ and hydrotalcite $[Mg_6Al_2(CO_3)(OH)_{16}4H_2O]$ phases which transformed to pure spinel phase at ~900°C by the decomposition of hydrotalcite at lower temperatures (400–800°C) and a solid-state reaction between MgO (decomposed from hydrotalcite) and $\gamma$-$Al_2O_3$ (derived from ammonium dawsonite hydrate) at higher temperatures (800–900°C). Ultrafine ($<100$ nm) spinel powders were obtained by calcining the precursor in the temperature range of 900–1200°C. The effect of calcination temperature on particle morphology and sinterability of the resultant spinel powders were investigated. Dense spinel ceramics (~99%) were obtained by sintering under vacuum at 1550°C for 2 h, using the powder calcined at 1100°C.

## Acknowledgements

One of the authors, J.-G. Li, would like to express his thanks to JISTEC/JST of Japan for granting an STA fellowship.

## References

[1] M. Sindel, N.A. Travitzky, N. Claussen, Influence of magnesium–aluminum spinel on the directed oxidation of molten aluminum alloys, Journal of the American Ceramic Society 73 (9) (1990) 2615–2618.

[2] G. Baudin, R. Martinez, P. Pena, High-temperature mechanical behavior of stoichiometric magnesium spinel, Journal of the American Ceramic Society 78 (7) (1995) 1857–1862.

[3] J.E. Sheehan, J. Sigalovsty, J.S. Haggerty, J.R. Porter, Mechanical properties of $MgAl_2O_4$ single crystal fibers, Ceramic Engineering and Science Proceedings 14 (7-8) (1993) 660–670.

[4] D. Lepkova, A. Batarjav, B. Samuneva, Y. Ivanova, L. Georgieva, Preparation and properties of ceramics from magnesium spinel by sol–gel technology, Journal of Materials Science 26 (1991) 4861–4864.

[5] P. Hing, Fabrication of translucent magnesium aluminate spinel and its compatibility in sodium vapors, Journal of Materials Science 11 (1976) 1919–1926.

[6] J.T. Bailey, R. Russell Jr., Sintered spinel ceramics, Ceramic Bulletin 47 (11) (1968) 1025–1029.

[7] R.J. Bratton, Coprecipitates yielding $MgAl_2O_4$ spinel powders, Ceramic Bulletin 48 (8) (1969) 759–762.

[8] J. Katanic-Popovic, N. Miljevic, S. Zec, Spinel formation from coprecipitated gel, Ceramics International 17 (1991) 49–52.

[9] S. Hokazono, K. Manako, A. Kato, The sintering behavior of

spinel powders produced by a homogeneous precipitation technique, British Ceramic Transaction and Journal 91 (1992) 77–79.

[10] M. Barj, J.F. Bocquet, K. Chhor, C. Pommier, Submicronic $MgAl_2O_4$ powder synthesis in supercritical ethanol, Journal of Materials Science 27 (1992) 2187–2192.

[11] O. Yamaguchi, H. Omaki, K. Shimizu, Formation of spinel hydroxides prepared by alkoxy-method, Journal of the Japan Society of Powder and Powder Metallurgy 22 (6) (1975) 202–204.

[12] T. Shiono, K. Shiono, K. Miyamoto, G. Pezzotti, Synthesis and characterization of $MgAl_2O_4$ spinel powder from a heterogeneous alkoxide solution containing fine MgO powder, Journal of the American Ceramic Society 83 (1) (2000) 235–237.

[13] O. Varnier, N. Hovnanian, A. Larbot, P Bergez, L. Cot, J. Charpin, Sol–gel synthesis of magnesium aluminum spinel from a heterometallic alkoxide, Materials Research Bulletin 29 (5) (1994) 479–488.

[14] J.-F. Pasquier, S. Komarneni, R. Roy, Synthesis of $MgAl_2O_4$ spinel: seeding effects on formation temperature, Journal of Materials Science 26 (1991) 3797–3802.

[15] Y. Suyama, A. Kato, Characterization and sintering of Mg–Al spinel prepared by spray-pyrolysis technique, Ceramics International 8 (1) (1982) 17–21.

[16] V. Montouillout, D. Massiot, A. Douy, J.P. Coutures, Characterization of $MgAl_2O_4$ precursor powders prepared by aqueous route, Journal of the American Ceramic Society 82 (12) (1999) 3299–3304.

[17] C.-T. Wang, L.-S. Lin, S.-J. Yang, Preparation of $MgAl_2O_4$ spinel powders via freeze-drying of alkoxide precursors, Journal of the American Ceramic Society 75 (8) (1992) 2240–2243.

[18] Z. Nakagawa, K. Hamano, M. Sakaguchi, S. Kanzaki, Characterization and sinterability of Mg–Al spinel powders prepared with a thermal decomposition of a freeze-dried sulfate, Yogyo-Kyokai-shi 90 (6) (1982) 313–319.

[19] A.K. Adak, S.K. Saha, P. Pramanik, Synthesis and characterization of $MgAl_2O_4$ spinel by PVA evaporation technique, Journal of Materials Science Letters 16 (1997) 234–235.

[20] C.R. Bickmore, K.F. Waldner, D.R. Treadwell, R.M. Laine, Ultrafine spinel powders by flame spray pyrolysis of a magnesium aluminum double alkoxide, Journal of the American Ceramic Society 79 (5) (1996) 1419–1423.

[21] S. Bhaduri, S.B. Bhaduri, K.A. Prisbrey, Auto ignition synthesis of nanocrystalline $MgAl_2O_4$ and related nanocomposites, Journal of Materials Research 14 (9) (1999) 3571–3580.

[22] R.J. Bratton, Characterization and sintering of reactive $MgAl_2O_4$ spinel, Ceramic Bulletin 48 (11) (1969) 1069–1075.

[23] R.J. Bratton, Sintering and grain-growth kinetics of $MgAl_2O_4$, Journal of the American Ceramic Society 54 (3) (1971) 141–143.

[24] T. Iga, Y. Isawa, High purity, fine $\alpha$-alumina powder obtained by thermal decomposition of ammonium dawsonite, in: S. Somiya, M. Agata, Y. Agata (Eds.), Transactions of the Materials Research Society of Japan, Vol. 11, Materials Research Society of Japan, Tokyo, 1991, pp. 1–12.

[25] S. Matsuda, Jpn Patent 1405552, 17 March 1987.

[26] J.-G. Li, J.-H. Lee, T. Ikegami, T. Mori, Low-temperature fabrication of transparent yttrium aluminum garnet (YAG) ceramics without additives, Journal of the American Ceramic Society, in press.

[27] S. Kato, T. Iga, S. Hatano, Y. Isawa, Synthesis of $NH_4AlO(OH)HCO_3$, Yogyo-Kyokai-Shi 84 (1976) 215–220.

[28] J.-G. Li, T. Ikegami, J.-H. Lee, T. Mori, Y. Yajima, Synthesis of Mg/Al spinel powder via precipitation using ammonium bicarbonate as the precipitant, unpublished work.

[29] M.J. Hudson, S. Carlino, D.C. Apperley, Thermal conversion of a layered (Mg/Al) double hydroxide to the oxide, Journal of Materials Chemistry 5 (2) (1995) 323–329.

[30] K. Hayashi, S. Toyoda, H. Takebe, K. Morinaga, Phase transformation of alumina derived from ammonium aluminum carbonate hydroxide (AACH), Journal of the Ceramic Society of Japan 99 (7) (1991) 550–555.

[31] P.-L. Chen, I.-W. Chen, Sintering of fine oxide powders: I. microstructural evolution, Journal of the American Ceramic Society 79 (12) (1996) 3129–3141.

[32] W.H. Rhodes, Agglomerate and particle size effects on sintering yttria-stabilized zirconia, Journal of the American Ceramic Society 64 (1) (1981) 19–22.

[33] F.F. Lange, Powder processing science and technology for increased reliability, Journal of the American Ceramic Society 72 (1) (1989) 3–15.

[34] F.F. Lange, Sinterability of agglomerated powders, Journal of the American Ceramic Society 67 (2) (1984) 83–89.