Characterization and Formation Process of Spinel (MgAl_2O_4) Prepared by Alkoxide ($\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$) Method

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Multiorganometallic compounds made by modifying the synthetic method studied by Thomas were used to prepare high purity submicron-size MgAl_2O_4 powders. Hydrolytic decomposition of $\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$ and the subsequent calcination process produced submicron powders of MgAl_2O_4 of more than 99.98+ % purity : 50 Å to 100 Å at 800°C and about 0.1 μm at 1200°C, and with purity of 99.98+ % : The major contaminant was Si from silicon grease. Homogeneity and stoichiometry of the powders after calcination were studied by transmission electron microscopy and chemical analysis. X-ray and infrared analyses indicated that the formation process of MgAl_2O_4 from $\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$ depends strongly on the atmosphere in hydrolysis of $\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$ and the subsequent calcination temperature.

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複合アルコキシド ($\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$) からのスピネル (MgAl_2O_4) の 生成過程とその特性

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複合有機金属化合物を用いて高純度、超微粒子のスピネル粉、 MgAl_2O_4 を合成した。 $\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$ の合成はThomasにより開発された方法を改良し、水銀添加によって行った。 $\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$ の加水分解とそれに続く焼成過程により、スピネルの超微粒子ができた：粒径は800°Cで50 Åから100 Å、1200°Cで約0.1 μmであった。純度は99.98+ %であった。主な不純物はシリコングリースからのSiであった。焼成後の粉の均一性と化学量論性は透過型電子顕微鏡(TEM)と化学分析により決定した。X線及び赤外分析により、 $\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$ から MgAl_2O_4 が生成する過程は $\text{MgAl}_2(i\text{-OC}_3\text{H}_7)_8$ の加水分解時の雰囲気及びそれに続く焼成温度に依存することが分かった。

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1. Introduction

Spinel (MgAl_2O_4) is known as a promoting agent for sintering silicon nitride (Si_3N_4)¹⁾. The mechanical properties of the sintered- Si_3N_4 depends much upon the degree of uniformity in the constitution. To obtain the uniformity, ultraly fine powder is required. It is well known that the alkoxides are usefull for the preparation of fine powder²⁾⁻⁵⁾. And some authors are trying to prepare spinel fine powder from two kinds of alko-

xides (for example, Al isopropoxide and Mg methoxide or Mg isopropoxide)^{4), 5)}. The preparation from the two kinds of alkoxides, however, seems to be less desirable to get fine powder than that from a double alkoxide containing Al and Mg, in which Mg and Al are located near to each other.

In the present work, formation of Mg-Al stoichiometrical spinel prepared from a double alkoxide was studied by modifying the method

described by Thomas²⁾. The white powder obtained by hydrolysis of double alkoxide was calcined at various temperature and was studied by means of IR, X-ray diffraction, transmission electron micrograph (TEM) and other analytical methods.

2. Experimental

2.1 Synthesis and analysis of Mg-Al alkoxide

Magnesium di-aluminium octaisopropoxide (Mg-Al alkoxide) was made by modifying the method described by Thomas^{2),3)}, in which mercury dichloride is used as catalyst. Basic equation for the modified reaction is as follows :

The magnesium metal powder of the purity of 99.9% and the aluminium triisopropoxide of reagent grade were used as-received. The isopropylalcohol of reagent grade was dried over synthetic zeolite and was decanted. Mercury dichloride was of reagent grade. The preparation of Mg-Al alkoxide was carried out in a glove box filled with water-free argon (<10 ppm H₂O). After 60 hours' reflux, their compounds were separated from raw materials, such as isopropylalcohol and aluminium triisopropoxide by distillation under reduced pressure of ca. 270 Pa. The products in the temperature range of about 125°C to 159°C were confirmed to be magnesium di-aluminium octaisopropoxide (Mg-Al alkoxide) from their IR spectrum (Fig. 1) and ¹H-NMR

Fig. 1. IR spectrum of Mg-Al alkoxide.
IR condition, sampling method : Liquid method, Cell : 0.2 mm of fixed NaCl-window, Concentration of Mg-Al alkoxide : ca. 2.5 wt%/CCl₄.
Peak No. : Wavenumber (cm⁻¹) : 1 : 2966, 2 : 2929, 3 : 2866, 4 : 2629, 5 : 1464, 6 : 1383, 7 : 1373, 8 : 1360, 9 : 1188, 10 : 1169, 11 : 1138, 12 : 1036, 13 : 976, 14 : 951, 15 : 837

Table 1. NMR data of Mg-Al alkoxide (50 wt%CDCl₃ soln. TMS standard).

¹ H NMR		
Chemical shift (ppm)	4.14	1.21
Assignment	α -Hydrogen	Methyl
Relative no. of Protons	1.0	6.1

Table 2. Analytical data of Mg-Al alkoxide.

Weight loss * (wt%)		Mg / Al ratio **	
Experimental Value	Theoretical Value	Experimental Value	Theoretical Value
25.95	25.84	1.00/2.00	1 / 2

* Weight loss of Mg-Al alkoxide (hydrolyzed in air, dried at 120 °C and calcined at 800°C)

** ICP emission data

spectrum (Table 1), and from ICP emission and the weight loss data for products obtained through hydrolysis of Mg-Al alkoxide and calcination of its hydroxide product (Table 2).

2.2 Preparation of spinel powder

(1) Preparation of A-series powders

20 g of Mg-Al alkoxide was dissolved in a mixture of benzene and ethylalcohol in ratio 1 : 1 under the atmosphere of argon. The solution was stirred well for 30 min in air. Stirring the solution for subsequent 20 min, 100 g of deionized distilled water was added dropwise to the solution which was being stirred. The solution was allowed to stirring for 60 min. White powders were precipitated from the solution as a result of the hydrolytic decomposition of Mg-Al alkoxide. The powders were filtered, and were kept in a vacuum drying oven at 90°C for 7 d (A-90). The powders (A-90) were then calcinated in the porcelain crucible under air for 60 min at 200°C (A-200), 400°C (A-400), 600°C (A-600), 700°C (A-700), 800°C (A-800), 1000°C (A-1000) and for 120 min at 1200°C (A-1200) and 1400°C (A-1400).

(2) Preparation of B-series powders

20 g of Mg-Al alkoxide was dissolved in 300 ml of *n*-hexane under the atmosphere of argon. The solution was refluxed for 60 min with vigorous stirring in argon. Stirring the solution for subsequent 20 min, 100 g of deionized distilled water was added dropwise to the solution which was being stirred. The solution was allowed to stir-

ring for 3 h. White powders were precipitated from the solution as a result of the hydrolytic decomposition of the alkoxide. The powders were filtered, and were kept in a vacuum drying oven at 120°C for 6 d (B-120). The powders (B-120) were then calcined in the porcelain crucible under nitrogen for 120 min at 400°C (B-400), 600°C (B-600) and 800°C (B-800).

2.3 Analysis of the powders

Impurities in the powders were detected with ICP emission spectroscopic analyzer. Amounts of residual carbon in the powders formed from organic alkoxide were determined through chemical analysis. Specific surface area of the powders was measured with a BET method using nitrogen adsorption after the powders were dried at 200°C in vacuum. The shape and size of the powders were determined with TEM. Infrared analysis and X-ray diffraction (with cobalt radiation and an iron filter) were applied to study the spinel-forming process.

3. Results and discussion

3.1 Emission spectroscopy

The emission analysis revealed that the agents were of purity of 99.98 + % (Table 3): the major contaminant was Si. As raw materials were free from Si, the impurity is thought to come from silicon grease used for sealing.

3.2 Properties of the powders

Hydrolytic conditions, calcination ones, colors, the amounts of carbon residue and specific surface area of the powders are given in Table 4. The results show that the amount of residual carbon and specific surface area of the powders are decreased as the calcination temperature is elevated under air (Table 4). Color of the powders is white with the exception of A-600,

Table 4. Color, C-residue and specific surface area of the powders.

no.	color	C-residue (%)	specific surface area (m ² /g)
A- 90	white	2.43	322
A- 200	white	2.05	334
A- 400	white	1.66	277
A- 600	gray	1.33	272
A- 700	white	1.14	307
A- 800	white	0.70	175
A-1000	white	0.30	65
A-1200	white	0.16	1.2
A-1400	white	0.02	0.03
B- 120	white	1.10	350
B- 400	white	0.84	327
B- 600	white	0.54	233
B- 800	white	0.31	140

which is gray. It suggests that the residual organic compounds turned to free carbon in the calcination of the temperature of ca. 600°C. Color of B-600, however, is white, suggesting remaining no free carbon in B-600.

3.3 Size and shape of the powders

TEM photographs of several powders are shown in Fig. 2. A-200 and A-600 consist of flaky particles (Figs. 2(a), (b)). In A-800 powder, some aggregations of spinel crystals of the size of 50-100 Å are observed and moreover moiré pattern is observed in some of the particles, which proves that the powders are crystalline (Fig. 2(c))⁶. A-1200 is less than 0.1 μm (Fig. 2(d)), which is, unexpectedly, nearly the same as that produced from the mixture of the two kinds of single alkoxides (Al isopropoxide and Mg isopropoxide)⁵. The calcination of the double alkoxides by spray pyrolysis in hot air blow would give finer powder than that of the mixture of two single alkoxides. B-400 consists of flaky particles which are similar to A-200 or A-600 (Fig. 2(e)). In B-600 and B-800, a long moiré pattern running through many particles are seen (Fig. 2(f), (g)), which proves that they are constructed from thin layers of crystallites of preferred orientation⁶. The crystalline size is of about 50 Å. The order of orientation of B-800 is higher than of B-600. The aggregation size was about the same as that of A-series powder.

3.4 Infrared spectra studies

The infrared spectra of A-series powders are

Table 3. Emission Spectrographic Analysis (in ppm) of Typical A-series powders and B-series ones.

Element	A- 90	A- 1200	B- 120	B- 800
Si	100	100	100	100
Fe	70	70	70	70
Ni	nd < 3	< 10	nd < 3	< 10
Mn	nd < 3	< 10	nd < 3	< 10
Pb	nd < 3	nd < 3	nd < 3	< 10
B	nd < 3	< 10	nd < 3	nd < 3
V	nd < 3	nd < 3	nd < 3	< 10
Cu	nd < 3	< 20	nd < 3	< 30
Ga	nd < 3	nd < 3	nd < 3	< 10

nd < = Not detected less than

Fig. 2. TEM photograph of several powders.
 (a) : A-200, (b) : A-600, (c) : A-800, (d) : A-1200,
 (e) : B-400, (f) : B-600, (g) : B-800

shown in Fig. 3. It was difficult to assign C-H stretch of some products from organic precursor. O-H stretches occur at ca. 3494 cm^{-1} (peak 1) and at ca. 1628 cm^{-1} (peak 2) and carbonate $\begin{smallmatrix} \text{O} \\ \diagup \text{C} \diagdown \\ \text{O} \end{smallmatrix}$ or O-C $\begin{smallmatrix} \text{O} \\ \diagup \text{C} \diagdown \\ \text{O} \end{smallmatrix}$ gives absorption peaks at ca. 1519 cm^{-1} (peak 3) and at ca. 1396 cm^{-1} (peak 4). M-O stretches of spinel, MgAl_2O_4 , occur at ca. 700 cm^{-1} (peak 8) and at ca. 526 cm^{-1} (peak 10). It is thought that the peaks, 5, 6, 7, 9, and 11,

Fig. 3. IR spectra of A-series powders.
IR condition, sampling method: KBr disc method,
Concentration of powder: ca. 0.3 mg/200 mg of KBr
Peak No.: Wavenumber (cm^{-1}); 1: 3494, 2: 1628, 3:
1518, 4: 1396, 5: 1074, 6: 870, 7: 784, 8: 700, 9:
623, 10: 526, 11: 472

would be given by Mg-containing γ -alumina-like structure. As calcination temperature is gradually elevated, the intensity of peaks 9 and 11 decreases gradually and disappears at the calcination temperature of ca. 600°C , while peaks, 8 and 10, given from spinel, come to appear simultaneously at the calcination temperature of 700°C . With further elevation of the calcination temperature, intensity of M-O stretches, given from spinel (MgAl_2O_4), increases, and that of O-H radicals and carbonate ones decreases gradually. These radicals remain in A-1000, after the as-prepared powder (A-90) is calcined at for 2 h. The infrared spectrum of A-1200 shows that the formation of spinel structure occurs without O-H radical or carbonate one. These show that the formation of pure spinel needs the calcination above the temperature of 1200°C . The infrared spectra of B-series powders are shown in Fig. 4. Compared with the intensity of peaks 3 and 4 occurring in A-series powders, that in B-series powders is very small, and peaks 3 and 4 are absent in B-800, which shows that B-800 do not contain carbonate radical. The spectrum of B-800, however, shows that the powder still contains a little O-H radical.

3.5 X-ray diffraction studies

The X-ray diffraction patterns of A-series pow-

Fig. 4. IR spectra of B-series powders.
IR condition is the same with that of Fig. 3. Wavenum-
ber of peak No. is the same with that of Fig. 3.

Fig. 5. X-ray diffraction patterns of A-series powders.

ders are recorded using a diffractometer with cobalt radiation and an iron filter, and are shown in Fig. 5. In A-90, very broad and unsymmetrical peaks appear in the range of diffraction angle from 38° to 56° in 2θ . These peaks are considered to correspond to (311) and (400) of spinel structure (Mg-containing γ -alumina-like amorphous) and the broad peak from 77° to 78° in 2θ is considered to correspond to (440) of the same structure, and it is thought that other several broad peaks ranging from 28° to 36° in 2θ , from 57° to 61° and from 70° to 75° come from double metal hydroxide (eg. $\text{Mg} \leftarrow \text{O} - \text{Al}$) or double metal carbonate (eg.

frared spectra in Fig.3. As the calcination temperature is elevated from 200°C to 400°C, the peaks, ranging from 28° to 36° in 2θ , from 57° to 61° and from 70° to 75°, become apparently small in the intensity, and in A-600 these peaks almost disappear. In the calcination temperature from 700°C to 1200°C, all peaks corresponding to MgAl_2O_4 are observed and the intensities increase with the calcination temperature. The X-ray diffraction patterns of B-series powders are shown in Fig.6. In B-120, lattice planes of (020), (120), (140 or 031), (051), (231) and (251) of boehmite structure, shifts a little to lower diffraction angle in compared with that of boehmite structure. It would be due to containing O-H radical or magnesium-containing parts. Also several unknown peaks ranging from 22° to 24° in 2θ , from 24° to 29.8°, from 38° to 42°, from 51° to 55° and from 70° to 74° are present in B-120.

Fig. 6. X-ray diffraction patterns of B-series powders.
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Fig. 7. Effect of calcination temperature on mean particle size of calcined powders.
Half width of diffraction peak in the diffraction angle of ca. 77.5° in 2θ , was used to calculate the mean particle size.

○ : A-series, ● : B-series

These peaks are considered to be attributed to $\text{MgAl}_2(\text{OH})_8$. As calcination temperature is elevated from 400°C to 600°C, all peaks which are considered to be attributed to boehmite and $\text{MgAl}_2(\text{OH})_8$ disappear and diffraction of (220), (311), (400) and (440) attributable to spinel structure (Mg-containing γ -alumina-like structure) appear (B-400, B-600). In B-800, the observed peaks are all attributed to MgAl_2O_4 .

The mean particle diameter of A-series powders and B-series ones was calculated using Scherrer's formular. For that calculation, the diffraction occurring at 77.5° (440) of spinel was used. The calculated values are shown in Fig. 7. The mean particle size of the calcined powders at 600°C or below (A-90 - A-600, B-120 - B-600) is 50 Å or less. According to TEM observation of A-200, A-600 or B-400, however, it is shown that it consists of many flaky particles (Figs. 2 (a), (b), (e)). According to TEM observation of B-600 or B-800, it is shown that it consists of thin layers of the oriented crystallines (Figs. 2(f), (g)). Therefore, the mean particle size of these powders can not be given correctly. The mean particle size of A-700 increases largely to 79 Å, which means that crystallization of MgAl_2O_4 occur at the calcination temperature of 700°C.

The specific surface area becomes smaller in good agreement with the tendency of the variation in grain size determined by Scherrer's formular.

As calcination temperature is further elevated, the mean particle size increases rapidly. For example, the mean particle size of A-1200 becomes 710 Å at 1200°C, which is much larger than that (104 Å or 203 Å) at 800°C or 1000°C.

As discussed above, the formation process of MgAl_2O_4 much depends on the way of hydration of Mg-Al alkoxide. In the hydrolysis of Mg-Al alkoxide in inert gas, Mg-Al alkoxide produces boehmite-like structure, and MgAl_2O_4 is considered to be produced in the succeeding calcination process via Mg-containing γ -alumina-like structure, as follows :

MgAl₂O₄

On the other hand, in the hydrolysis of Mg-Al alkoxide in air, different compounds seem to be produced, which will be resulted from the prevention of debonding of $\text{Mg} \begin{smallmatrix} \text{O} \\ \swarrow \searrow \end{smallmatrix}$ caused by the formation of carbonate. And the formation process will be expressed as follows :

↓ +H₂O, in air

↓ calcination in air

where $4 > x, y \gg z$

Partly, spinel (Mg-containing γ -alumina-like

↓ amorphous)

↓ calcination in air

4. Conclusion

Hydrolytic decomposition of MgAl₂(*i*-OC₃H₇)₈ and the succeeding calcination process produced powders of MgAl₂O₄ with particle sizes of submicron : 50 Å to 100 Å at 800°C and about 0.1 μm at 1200°C. The size of aggregated powder of 0.1 μm was about the same as that of the powders produced from the two kinds of alkoxides (Al

isopropoxide and Mg isopropoxide). The produced powders of MgAl₂O₄ analysed purity of 99.98+ % : the major contaminant was Si from silicon grease. The formation process of MgAl₂O₄ from MgAl₂(*i*-OC₃H₇)₈ depends on the atmosphere in hydrolysis of MgAl₂(*i*-OC₃H₇)₈, and under inert gas, it turned to powders of boehmite-like structure, but under air, different compounds seem to be produced because of the influence of CO₂ in air. Anyway in the succeeding calcination process, they turned to high-purity submicron particulates of MgAl₂O₄ via Mg-containing γ -alumina-like structure.

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References

- 1) Hideyuki Masaki, Japan Patents 919413 (Jan. 29, 1977).
- 2) Ian M. Thomas, US Patents 3761500 (Sept. 25, 1973).
- 3) Ian M. Thomas, US Patents 3786137 (Jan. 15, 1974).
- 4) Yoshiharu Ozaki and Masaaki Hidejima, Proceedings of the Annual Meeting of Yogyo-Kyokai, 108 (1978).
- 5) Tomonori Takahashi, Minoru Matsui and Isao Oda, *ibid.*, 137-38 (1982).
- 6) N. F. Mott, "Advances in Physics, 7", 328-46(1958).