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Short communication

SYNTHESIS AND FORMATION MECHANISM OF SPINEL FROM HETEROGENEOUS ALKOXIDE SOLUTION

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1 INTRODUCTION

$MgAl_2O_4$ spinel is expected to be a promising constructural material at high temperatures, because of the superior mechanical, chemical and thermal properties. However, few studies on polycrystalline spinel have been carried out compared with on the single crystal, because it is very difficult to produce the dense polycrystalline spinel using powders prepared by conventional methods. In order to improve its sinterability, the synthesis of fine spinel powders has been tried by advanced techniques such as sol-gel[1],[2], freeze-drying[3],[4], coprecipitation[5],[6] and so on.

Authors[7] have successfully synthesized spinel powders with good sinterability from heterogeneous alkoxide solution including very fine MgO powders. In the present study, the formation mechanism of spinel phase from the precursors was studied.

2 EXPERIMENTAL

2.1 Preparation of spinel precursors

Preparation of spinel precursors is schematically given in Fig.1. Aluminium isopropoxide and MgO powders (Ube Chemical Industries Co. Ltd.) were used as starting materials. The mean diameter of MgO was very fine, 10nm and its purity was 99.98%. Aluminium isopropoxide was dissolved in isopropanol at the molar ratio of alkoxide : alcohol = 1 : 20 and refluxed for 2h. After MgO powder was added to the solution, further refluxing was carried out for 2h to get the solution well-dispersed with MgO. And H_2O was added to the solution to promote gelation. The obtained gel was evaporated in vacuum at 50°C to remove extra alcohol and H_2O. The precursor was kept at 80°C in drying oven.

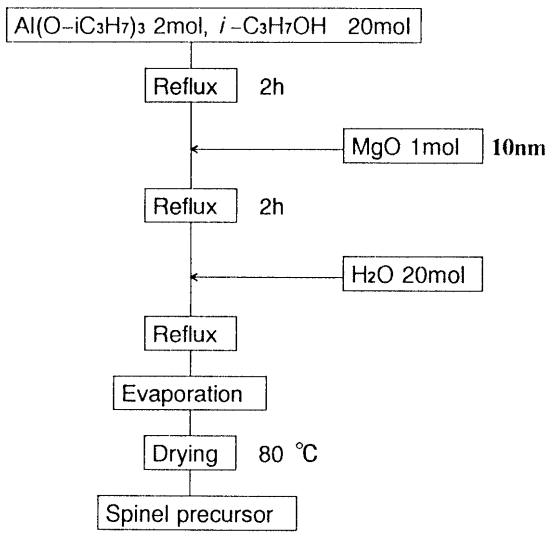

Fig.1. Procedure of preparing spinel precursors.

2.2 Chracterization of spinel precursors and powders

The obtained spinel precursors were calcined at various temperatures from 400°C to 1200°C for 1h. The crystalline phase was identified by X-ray dffraction(XRD) analysis, using Ni-filtered CuKα radiation. The thermal behavior of precursors was examined by DTA and TGA. The thermal analysis was carried out at a heating rate of 5°C/min under flowing dried air of 100ml/min. Morphorgy of particle in precursors and calcined powders was observed by SEM.

3 RESULTS AND DISCUSSION

The spinel precursors were found to be composed of boemite (AlO(OH)) and Mg-Al mixed-hydroxide ($Mg_4Al_2(OH)_{14}\cdot 3H_2O$) by XRD analysis. Yamaguchi et al.[1] prepared spinel precursors by sol-gel technique, using only metal alkoxides as starting materials; aluminium isoamyloxide and magnesium isoamyloxide. They also reported that their precursors were composed of boemite and the Mg-Al mixed-hydroxide. Even using MgO powders as a starting material, the same product as prepared with only alkoxides could be obtained.

Three distinct endothermic reactions were observed in DTA curve of the precursor and they could be identified as decomposition of crystal water and hydroxyl groups in the Mg-Al mixed-hydroxide. However, no distinct change owing to the formation of spinel phase could be recognized. And the weight loss was observed accompanied with the endothermic reaction.

The precursors were calcined at temperatures from 400°C to 1200°C to examine the formation mechanism of spinel phase. The change of phases as a function of calcining temperature is shown in Fig.2. The calcination up to 400°C made diffraction peaks of boemite

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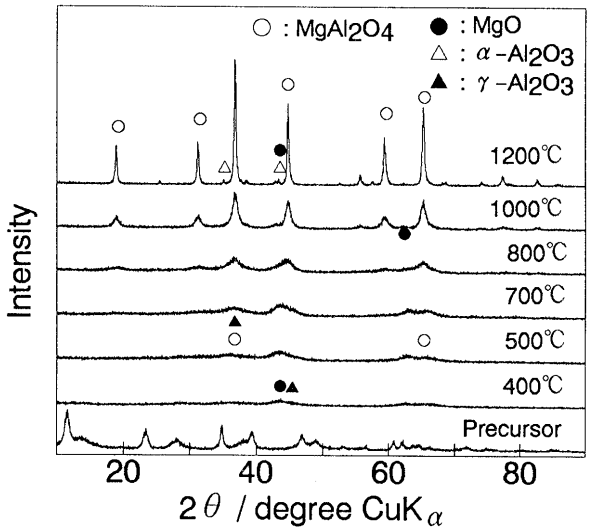

Fig.2. Effect of calcining temperature on crystalline phases for powders prepared with $H_2O/MgO=20$.

and the Mg-Al mixed-hydroxide disappeared gradually. The original peaks could not be recognized at 400°C and broad peaks were found instead of them. They were identified to be diffractions of γ-Al_2O_3 transformed from boemite and MgO resulting from the thermal decomposition of the mixed-hydroxide. The reaction is shown as follows.

$$Mg_4Al_2(OH)_{14}\cdot 3H_2O = MgAl_2O_4 + 3MgO + 10H_2O$$

Considering the equation, the decomposition of the mixed-hydroxide should also produce spinel, accompanied with the formation of MgO. However, diffraction peaks of spinel phase could not be recognized at 400°C, because the crystallite size of spinel would be very small. With the increase of calcining temperature, the peaks of spinel appeared and became large and sharp due to the grain growth. α-Al_2O_3 could not be detected up to 1200°C. That is, the formation of spinel phase would be proceeded by the reaction between γ-Al_2O_3 from boemite and MgO from the decomposition of the mixed-hydroxide. However, the monolithic spinel phase could not be obtained at a temperature lower than 1200°C. Reactivity of precursors is needed to be enhanced further.

Figure 3 shows SEM photographs of spinel precursor and calcined powders. Needle-like crystals were observed in precursors. They were inferred to be boemite because of its crystal structure and XRD analysis as shown in Fig.2. And very fine primary particles aggregated each other. In the case of calcining at 400°C, the particles became finer than the precursors. This temperature was corresponding to the beginning of decomposition of the mixed-hydroxide. And increase of the temperature made the particle size larger. Fine and uniform particles could be obtained even at a calcining temperature of 1200°C. Specific surface area of the spinel powder calcined

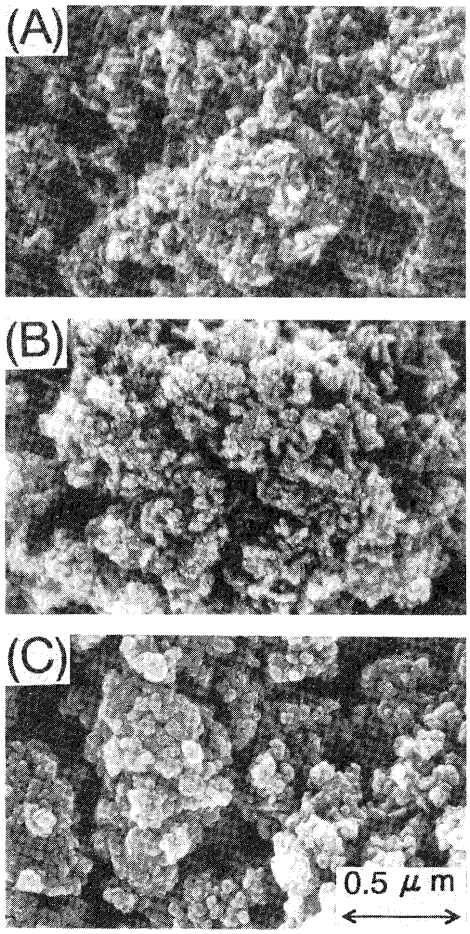

Fig.3. SEM photographs of spinel precursor (A) and powders calcined at 400°C (B) and 1200°C (C).

at 1200°C was approximately $38m^2/g$. The calcined powders are considered to be very reactive.

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