Preparation and Thermal Behavior of Monodispersed Al₂O₃-TiO₂ Powder Synthesized by Alkoxide Method

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Monodispersed Al_2O_3-TiO_2 powder was prepared by metal-alkoxide hydrolysis. A homogeneous nucleation/growth occurred in the solutions containing ethanol, butanol and acetonitrile, and resulted in spherical, submicrometer-sized powder. The titania and the alumina crystals were formed at 800°C and 1000°C, respectively. These crystals were subsequently reacted each other beyond 1320°C and formed Al_2TiO_5. The relative densities of sintered bodies prepared with as-received powder were examined at the temperature range of 1300~1500°C and they were about 79% at 1300°C. The formation of aluminum titanate decreased the relative density at the temperature range of 1300~1450°C, and at above 1450°C, the relative density started to increase again. It was observed that α-Al_2O_3-doped aluminum titanate was more stable than pure aluminum titanate at 1200°C.

Key words : Alkoxide, Al_2O_3-TiO_2 powder, Hydrolysis, Monodispersion, Thermal stability

I. Introduction

It is well known that high quality powders are essential for the development of high technology ceramic materials. Therefore, starting powder needs to be controlled in the light of morphology, size distribution and purity, etc. Numerous works have been conducted to satisfy the required quality. The prerequisite conditions of powder to be the defect-free ceramics are submicrometer-size and the narrow particle-size distribution of less than 10% from the average particle size.[1] Thus, the syntheses of various oxide powders pursuing the submicrometer and mono-sized were attempted.[2-5] Amongst the many candidate processings, an alkoxide method is one of the most promising ways. In 1950, LaMer and Dinegar described the theoretical bases for the monodispersed particles.[6] There are three steps in the theory. As the first step, if the supersaturation of reaction product reaches a critical value, the nucleation proceeds in a short time. In the second step, the supersaturation is lowered to a value of concentration in which the further nucleation is not possible. In the final step, the existing nuclei grow until the concentration decreases to the equilibrium concentration of system. The recent works on the preparation of alumina powder prepared by the hydrolysis of metal-alkoxide indicated that it is difficult to control the particle size. This is because the hydrolysis proceeds in a short time, and the particles show the tendency of agglomeration.[7] Thus, the alkoxide method still needs to be improved for successful powder preparation. Besides alumina, other systems were also studied. In the prevoius works for SiO_2, ZrO_2, Al_2O_3 powders, the longer the length of the carbon chain in alcohol, the more difficult to yield the mono-sized powder. In addition, the

reaction between H_2O and metal atoms can be retarded by the steric hindrance when the number of carbon branch in alcoholic solvent is increased, which results in the agglomeration and polydispersion. Thus, the alcohol containing less branches is required for a homogeneous nucleation and growth.[3,8,9] However, rapid reaction resulted from less carbon branches leads to the narrow size distribution but non-spherical particles are obtained. In this work, the condition for the powder synthesis in Al_2O_3-TiO_2 system was optimized with alkoxide method, and the phases and formation of aluminum titanate at various temperatures were studied.[12-15]

The relative densities and microstructures of sintered bodies made from as-prepared powder were studied at various temperatures. The previous works showed that the density of sintered body varies according to the calcination temperature of powder.[15] In this study, the relative density of sintered bodies which were obtained from as-prepared powder was measured at various temperatures. The formation of aluminum titanate leads to the increase of volume, which makes the sintered body porous. This phenomena occurred at the temperature range of 1300~1450°C and, at higher temperature, the body started to be densified.

It is reported that aluminum titanate was instable at about 1000~1300°C.[16] Many studies were done to suppress the thermal decomposition which restricts high temperature application. There are two ways for the stabilization of aluminum titanate. One is the thermodynamic way, in which MgO, Fe_2O_3, Cr_2O_3, GaO_2, etc. were added for the formation of solid solution with aluminum titanate. The other is the kinetic way, in which SiO_2, ZrO_2, α-alumina, mullite, etc. were inserted between Al_2TiO_5 grains to retard the movement of grain boundaries.[16,17] When we synthesized

the powders, powder composition was adjusted to Al_2O_3 : TiO_2=60 : 40 for the mechanical strength and the stability of aluminum titanate. The 20% surplus of Al_2O_3 affected the stability of aluminum titanate.

II. Experimental Procedure

1. Powder synthesis

Al(O-sec-C_4H_9)$_3$ and Ti(OC$_2$H$_5$)$_4$ were used as precursors of Al_2O_3 and TiO_2, respectively. The octanol, butanol, ethanol and acetonitrile were used as solvents. HPC (hydroxypropyl cellulose) was added to help the dispersion of particles. Al_2O_3-TiO_2. was synthesized using the procedure shown in Fig. 1. Firstly, two solutions were prepared. Those were the alkoxide solution consisting of various alcohols and Al-, Ti-alkoxide, and the hydrolytic solution containing H_2O, HPC and acetonitrile. For the mono-sized fine particles, the alkoxide and hydrolytic solutions were added and mixed using the magnetic stirrer at 70°C in N_2 atomosphere. The hydrolysis began within a few seconds, and the aging was performed for 30 min after 5 min mixing, and then powder and solvent were separated by centrifugation at 4500 rpm. Finally, the resulting powder was made by drying at 105°C for 24 hrs.

2. Characterization of powders

Morphology and size distribution of the particles were examined in SEM (JEOL, JSM-35CF) under the condition of 25 kV, 20 mA. EDS was used to conduct the quantitative analysis of Al_2O_3 and TiO_2. The crystallization of as-prepared powder and the phase transformation were investigated by XRD. And the thermal behavior of as-prepared powder was observed by monitoring the TG-DSC curve at the rate of 10°C/min.

3. Relative densities and microstructures of sintered bodies

Fig. 1. Experimental procedure for controlled hydrolysis of alkoxides.

Green bodies were made from as-prepared powder which was not calcined, under the conditions of 173 MPa C.I.P. after uniaxial pressing, and then, heat treated in the range of 1300~1500°C, with 10°C/min. Dwelling time was 1 hour at each temperature. At every 50°C, microstructures were investigated by SEM and, relative densities were measured in accordance with KS L 3114.

4. Thermal stabilities of aluminum titanate

The decomposition of sintered body (Al_2O_3 : TiO_2=60:40) was compared with pure aluminum titanate body (Al_2O_3 : TiO_2=50 : 50). The samples were prepared from powder by C.I.P. and sintered at 1600°C for 2 hours and then, quenched to room temperature. The samples were annealed at 1200°C for 1 h, 2 h, 3 h, 5 h, 10 h, respectively. The quantitative XRD analysis was used for the data on the decomposition of aluminum titanate to Al_2O_3 and TiO_2.

III. Results and Discussion

1. Synthesis of monodispersed composite powders

The influences of the amount of alkoxide, water and dispersant, and the composition of solvent on the morphology of composite powder were studied. The metal a-toms surrounded by carbon-branches in an alkoxide unit were hydrolyzed with the H_2O, and formed Oxo-bridges. For the uniformity in reaction, various solvents were used. The hydrolysis time was delayed by increasing the amount of butanol in solvent, and the resulting morphology of powder was changed from a monodispersed state to a polydispersed state. Therefore, for the synthesis of monodispersed powder, we used ethanol which has short branches. In fact, such choice enhanced the rate of hydrolysis/condensation. The optimum composition of solvent for monodispersion was 20 vol% of butanol and 30 vol% of ethanol, and the monodispersed powder was obtained at the water concentration of 0.02 mol/L. The extent of agglomeration, thus polydispersity, increases with increasing water content. This might be originated from the fact that high water concentration causes the partial and rapid nucleation/growth before homogenization of solution, and leads to the agglomerated polydispersion. On the other hand, if the water concentration is too low, e.g., below 0.02 mol/L, the nucleation occurs progressively rather than simultaneously, resulting in polydispersion.

Various forces act between synthesized particles.[18] Those are Van der Waals attraction, electrostatic repulsion, steric interaction and solvation energy, etc. The particles bond together to form agglomerates by the action of Van der Waals force. To prevent this agglomeration, these forces must be controlled. The particle contacted with the solution has surface charge, and 'the double layer' is formed on the surface of particles which cause the repulsive force by electrostatic in-
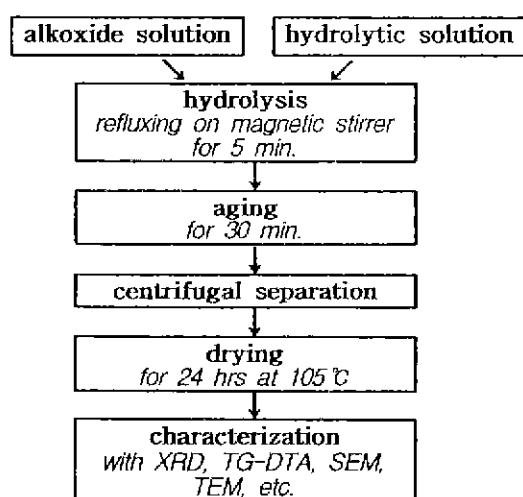
teraction between two overlapping electrical double layers. Controlling the kind and amount of electrolytes in solution can maximize the repulsion and limit the agglomeration.

However, in this work, we were able to prevent particles from agglomeration by formation of steric barrier which was originated from adsorption of polymer on the surface of synthesized particles. When adsorption layers are approached, the formation of steric barrier can be illustrated by the reduction of entropy and the increase of enthalpy. For this effect, the polymer must satisfy several prerequisite conditions. Firstly, adsorption layer must cover the surface of particles entirely, and the one end of polymer must adhere to the particle and the other end should be soluble in liquid. The adsorption layer needs to be thick enough to get out from Van der Waals attraction force.[5,10,11]

Considering these facts, we used HPC as a dispersant to prevent agglomeration by increasing* steric repulsion. The HPC concentration was balanced with 0.1 g/L in order not to form micelle. As a result, the monodispersed Al₂O₃-TiO₂ powder was obtained with the small amounts of butanol, alkoxides and water. We could separate the powder from the solvent by centrifugation. The optimum concentrations were indicated in the T-H4 of Table 1.

2. Morphology and phase analysis

SEM pictures in Fig. 2 show the various Al₂O₃-TiO₂ powders. The variation of morphology was demonstrated clearly. The shape and size of particles can be adjusted depending on the existence of dispersant, composition of solvent, concentration of reactants. The sample T-H4 showed a narrow distribution of particle size in the range of 0.2~0.4 μm which is close to monodispersion. An

Table 1. The Composition of Solutions for Al₂O₃-TiO₂ Powder

	Alkoxide Solution (vol. %)						Hydrolytic Solution (vol. %)		Morphology
	Al-alx (mol/L)	Ti-alx (mol/L)	Butanol	Ethanol	Octanol	HPC (g/L)	Acetonitrile	H₂O (mol/L)	
T-P1	0.05	0.05	25	25	0	0	50	0.2	agglomeration
T-P2						0.1			polydispersion
T-O1	0.05	0.05	20	20	10	0.1	50	0.2	gellation
T-O2								0.1	agglomeration
T-BE1	0.05	0.05	40	10	0	0.1	50	0.2	gellation
T-BE2			30	20					agglomeration
T-BE3			20	30					polydispersion
T-BE4			10	40					polydispersion
T-AT1	0.07	0.07	20	30	0	0.1	50	0.28	agglomeration
T-AT2	0.05	0.05						0.20	same with T-BE3
T-AT3	0.03	0.03						0.12	polydispersion
T-AT4	0.01	0.01						0.04	polydispersion
T-H1	0.01	0.01	20	30	0	0.1	50	0.12	agglomeration
T-H2								0.08	polydispersion
T-H3								0.04	same with T-AT4
T-H4								0.02	monodispersion

(a)   (b)   (c)
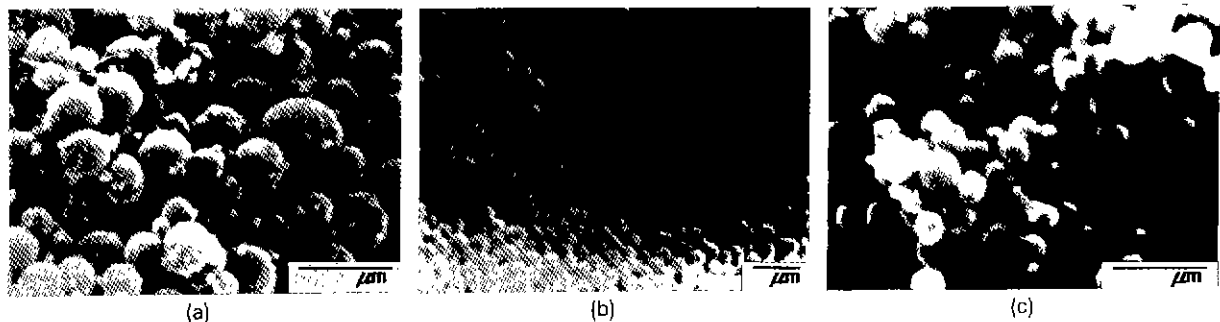
Fig. 2. SEM photographs of synthesized powders. (a) polydispersion (sample T-AT4). (b),(c) monodispersion (sample T-H4).

analysis of the phase transformation was performed by XRD as shown in Fig. 3. At first, the samples heat-treat-
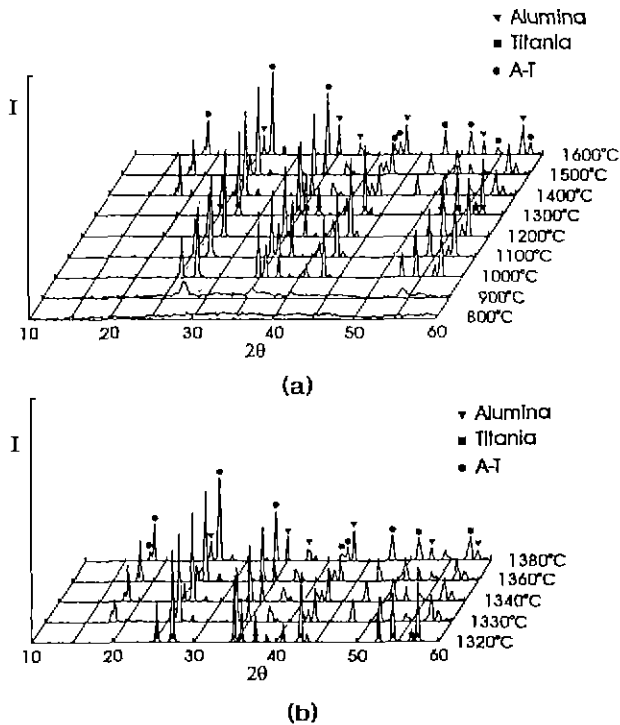

(a)

(b)

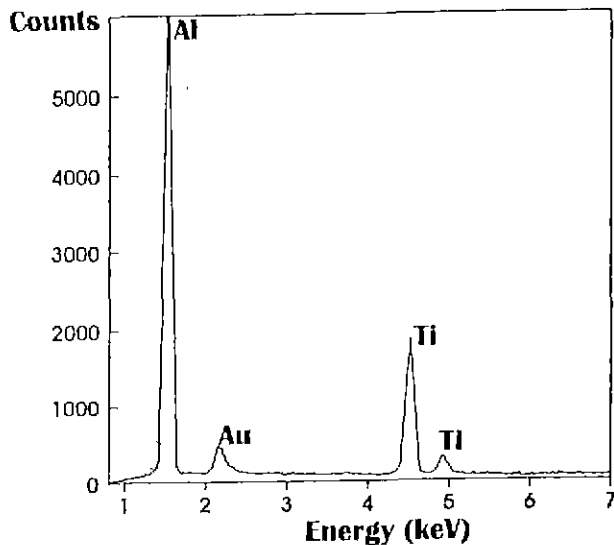**Fig. 3.** XRD patterns of Al_2O_3-TiO_2 powder. (a) measured at every 100°C. (b) measured at every 20°C.

Fig. 4. EDS analysis for Al_2O_3-TiO_2 powder.

Table 2. Composition Analysis by EDS

Element	%Element	Atom%			% Oxide
Al K	31.905	26.587		Al_2O_3	60.286
Ti K	23.814	11.178	oxide from ⇒	TiO_2	39.724
O K	44.290	62.236			
TOTAL	100.010	100.000			100.010

ed at every 100°C up to 1600°C were examined by XRD, and then from 1320°C at which the aluminum titanate started to appear, the samples heat-treated at every 20°C were investigated. In the case of Al_2O_3-TiO_2 powder, the crystallization of TiO_2 occurred at 800°C and α-Al_2O_3 phase appeared at 1000°C. Above the 1320°C, Al_2TiO_5 compound with ~20 vol% of α-Al_2O_3 was formed by the 1 to 1 reaction of Al_2O_3 with TiO_2, and the starting powder composition was analyzed by EDS as shown in Fig. 4 and Table 2. A broad endothermic peak which could result from dehydration appeared at near 100°C is shown in TG-DSC curve of Al_2O_3-TiO_2 powder (Fig. 5). A large exothermic peak at about 300°C might be originated from the combustions of residual solvent and organic contents. The exothermic peaks from crystallization of titania and alumina occurred at above 800°C and 1000°C, respectively. The endothermic peak near 1320°C could be observed due to the formation of Al_2TiO_5. These results agreed with XRD analysis. The TGA curve showed the total mass decrease of about 30%.

3. Relative densities and microstructures of sintered bodies

The microstructure after the sintering of green body was porous due to the evaporation of organic contents
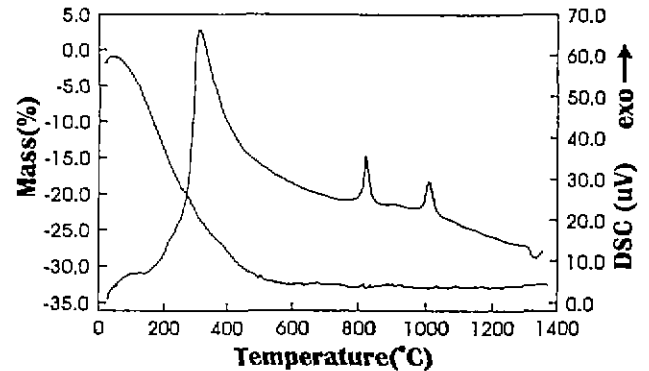

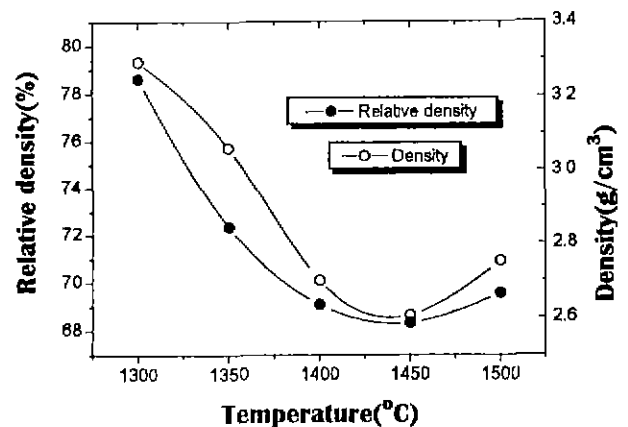**Fig. 5.** Thermal analysis by TG-DSC curve.

Fig. 6. Relative densities of sintered bodies.
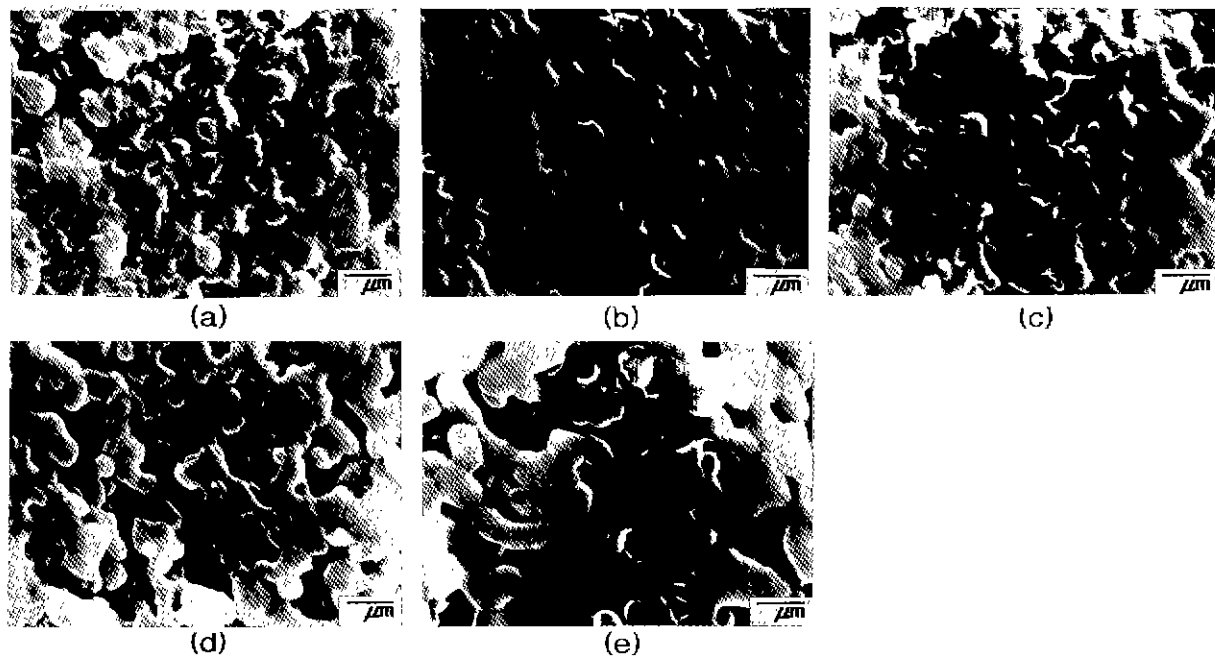
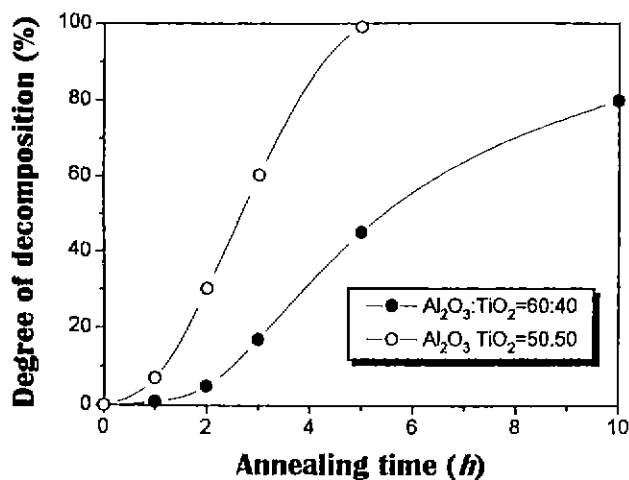Fig. 7. SEM photographs of bodies sintered at (a) 1300°C, (b) 1350°C, (c) 1400°C, (d) 1450°C and (e) 1500°C.

Fig. 8. Decomposition of Al_2TiO_5 at 1200°C.

and formation of aluminum titanate. At 1300°C, the relative density was about 79%. At above 1320°C where aluminum titanate is formed, 11% of volume expansion occurred. Up to 1450°C, the microstructure had opened with increasing the temperature by formation of Al_2TiO_5. Beyond that temperature, the density started to increase by densification, and these phenomena were shown in Fig. 6 and Fig. 7.

In the temperature range of 1300~1450°C the nucleation and growth of Al_2TiO_5 cell occurred in the unreacted Al_2O_3-TiO_2 matrix. In the body sintered at 1500°C, polyhedral α-Al_2O_3 existed either in the irregular Al_2TiO_5 grains or in the grain boundaries. Because of the thermal anisotropy of Al_2TiO_5, microcracks were observed in the quenched samples.

4. Stability of aluminum titanate

The mechanical properties of aluminum titanate are expected to be very poor since extensive microcracks due to the thermal mismatch are observed. Moreover, the material tends to decompose into ingredient oxides at the temperatures below 1250°C. This can limit the high temperature applications.

When the prepared powder was sintered, Al_2TiO_5 and surplus α-Al_2O_3 were formed by equimolar reaction of Al_2O_3 and TiO_2. Though a stabilizer was not added, this α-Al_2O_3 showed the effect on the thermal stability of aluminum titanate. For the comparision of stability between pure Al_2TiO_5 and α-Al_2O_3 doped Al_2TiO_5, the samples were annealed at 1200°C and the result was shown in Fig. 8. This α-Al_2O_3 showed an effect on kinetic stabilization in which the grain growth of Al_2TiO_5 was suppressed by second phase. However, long term stability was not improved significantly. Thus, further studies on this point are expected.

IV. Conclusions

1. The spherical and monodispersed fine Al_2O_3-TiO_2 powder was synthesized by the metal-alkoxides hydrolysis in an alcoholic solution.

2. The optimum condition for monodispersing Al_2O_3-TiO_2 powder was Al-alkoxide 0.01 mol/L, Ti-alkoxide 0.01 mol/L, Butanol 20 vol%, Ethanol 30 vol%, HPC 0.1 g/L, Acetonitrile 50 vol%, H_2O 0.02 mol/L.

3. Titania and alumina started to crystallize at 800°C, 1000°C, respectively in as-prepared Al_2O_3-TiO_2 powder, and aluminum titanate was formed at above 1320°C.

4. The relative density of sintered body which was ob-

tained from as-prepared powder and sintered at 1300°C was about 79%. It decreased with increasing the temperature and, increased again at above 1450°C by densification.

5. From the annealing test of sintered bodies which were obtained from $Al_2O_3 : TiO_2=60 : 40$ powder, it was shown that the thermal stability of Al_2TiO_5 was improved by the role of surplus α-Al_2O_3.

Acknowledgement

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