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Preparation of nano-structured ceramics using nanosized Al_2O_3 particles

H. NODA, K. MURAMOTO, H. KIM*
Department of Ecological Environment and Life Engineering, Toyohashi University of Technology, Tempaku-cho Toyohashi-shi Aichi-Ken 441-8580, Japan
E-mail: kim@eco.tut.ac.jp

This study is established with the theory that toughness of ceramics can be improved by reducing the grain sizes of alumina (Al_2O_3) ceramics. For nano-structured Al_2O_3 ceramics, nano-sized Al_2O_3 particles can be synthesized by MOCVD (metal organic chemical vapor deposition) method with $Al(CH_3)_3$. The synthesized particle sizes were 5.6, 11.2 and 22.4 nm, and these particles were used as initial materials. The grain sizes in nano-structured ceramics were controlled by both sintering temperature and holding time. They transformed dramatically from γ-Al_2O_3 to α-Al_2O_3 when sintered above 1223 K for two hours. The transformation temperature was lowered by 250 K in comparison the temperature of the phase transformation in bulk. The grain size of nano-structured alumina ceramics grew with increasing sintering temperature. At the sintering temperature of 1173 K, it is necessary of an incubation time for grain growth. The incubation time became longer while particle size decreased. After the incubation time, the rate of grain growth was steeply increased. Above 1273 K, the grain growth directly occurred without any incubation time.

1. Introduction

The materials with nano-structure have been given much attention in the possibility for functional materials of electrical parts and structural materials of mechanical parts. The ceramics with nano-structured grains has some special properties such as super plasticity [1, 2] and low sintering temperature [3, 4]. On the other hand, nano-sized particles could be prepared by MOCVD (metal organic chemical vapor deposition), CVC (Chemical Vapor Condensation) [5, 6], CF-CVC (Combustion Flame–Chemical Vapor Condensation) [7, 8] or sol-gel [9] methods. Among these methods, the MOCVD and CVC method is a promising candidate for structural materials, due to the possibility of mass-production of highly pure nano-sized particles with good uniformity in size.

Furthermore, during sintering process, it has been generally recognized that nano-structured ceramics are affected by various factors of the sintering process, such as sintering temperature, holding time and pressure [4, 10–14]. However, the relationships between grain growth and particle size for various sintering temperatures, holding times and pressures on nano-structured ceramics have not been reported yet.

This study was started to fabricate ceramics with high toughness and control the toughness by reducing the grain size in nano-structured ceramics. This grain size can be controlled by designating a particle size, by controlling a sintering temperature and by having an appropriate holding time.

In order to prepare the nano-structured alumina ceramics, some nano-sized Al_2O_3 particles were synthesized by MOCVD with $Al(CH_3)_3$, (Trimethyl Aluminum, TMA). The average sizes of particles were 5.6, 11.2 and 22.4 nm respectively. They were used as initial materials. The grain growth in the nano-structured ceramics was controlled by both sintering temperature and holding time.

2. Experimental method

The nanosized Al_2O_3 particles were prepared in a tube type thermal MOCVD system, which consists of bubbler, thermal reactor and filters. Fig. 1 shows the schematic diagram of the thermal MOCVD system used in this experiment. $Al(CH_3)_3$ (TMA) was used as raw material and was bubbled in the bubbler, and finally was carried into the reactor by He gas at a flow rate of 8.33×10^{-7} m^3/sec. The TMA concentration was changed from 0.011 to 0.182 mol% by controlling the evaporation temperature under Helium atmosphere. Helium and Oxygen gas flow rate were controlled by Mass Flow Controller (MFC). The flow rate of Oxygen gas was 3.33×10^{-6} m^3/sec. TMA and Oxygen was entered and reacted with each other in the thermal reactor. The conditions of reaction were 1273 K in temperature and 37 kPa in pressure. The synthesized Al_2O_3 particles were collected in the attached micro-filters. The crystalline phases were identified by X-ray diffraction (XRD, Rigaku RINT-2500) analysis using CuKα

*Author to whom all correspondence should be addressed.

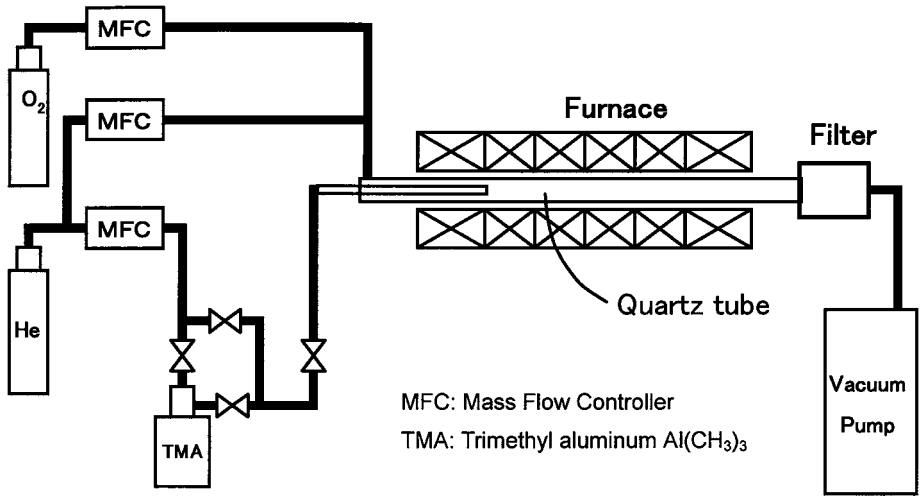


Figure 1 The schematic diagram of thermal MOCVD system.

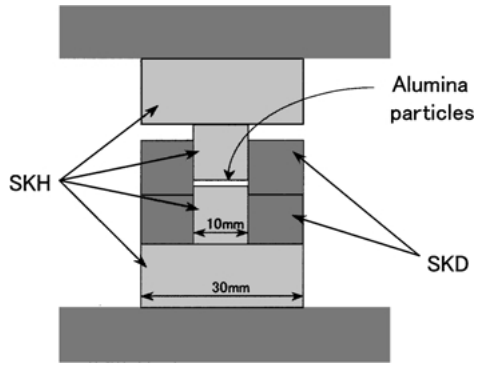


Figure 2 The schematic diagram of mold made by SKH and SKD steel.

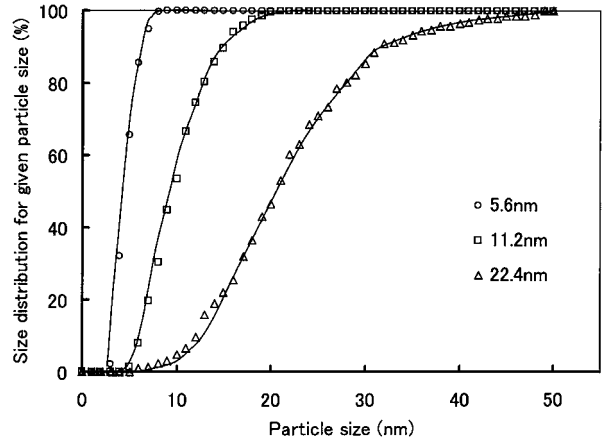


Figure 3 The particle size distribution of Al_2O_3 synthesized with O_2 reactant gas as a function of grain size.

radiation. The particle morphologies and sizes were determined by observation through transmission electron microscopy (TEM, HITACHI H-800).

Nano-sized Al_2O_3 particles were pelletized under the pressure of 2.5 GPa on a uniaxial direction for one minute. Fig. 2 shows the schematic diagram of the mold made by SKH and SKD steel. In order to investigate the effects of various particle sizes on sintering temperatures and holding times, the three different particle sizes were used as initial particles. All the initial particles had γ type crystal phases. The properties of the particles and the size distribution are shown in Table I and Fig. 3, respectively. The diameter and weight of the pelletized Al_2O_3 samples were 10 mm and 40 mg, respectively. These pelletized Al_2O_3 samples were sintered in the electric furnace. The sintering temperature varied from 1123 K to 1623 K. The holding time during sintering process also changed from the start to 16 hours.

TABLE I The properties of Al_2O_3 particles synthesized by CVD method

TMA concentration (mol%)	Average particle size (TEM) (nm)	Standard deviation (nm)	BET surface area (m^2/g)	Al_2O_3 phase
0.011	5.6	1.18	206	γ
0.066	11.2	3.57	128	γ
0.182	22.4	8.27	122	$\gamma + \delta$

The X-ray diffraction (XRD) was used for determining crystal phases. The average grain size in the sintered ceramics was estimated by Scherrer's equation from the XRD pattern and also observed by transmission electron microscopy.

3. Results and discussion

The particle sizes of the nano-sized Al_2O_3 particles were measured by TEM micrographs. Table I. shows the properties of the synthesized Al_2O_3 particles with various sizes. The crystal phase of the nano-sized Al_2O_3 particles below 11.2 nm was γ phase. When the particle size became 22.4 nm, the crystal phase γ and δ phases. The average size of Al_2O_3 particles decreased from 22.4 nm to 5.6 nm with decreasing the TMA concentration from 0.182 to 0.011 mol%. Also, the BET surface area decreased with increasing TMA concentration from 0.011 to 0.182 mol%. The relationship between the BET surface and the TMA concentration did not show linearity. Fig. 3 shows the particle size distribution of the nano-sized Al_2O_3 particles. The standard deviation was increased with increasing the particle size.

Figs 4 and 5 show the X-ray diffraction patterns of sintered Al_2O_3 ceramics and the grain sizes estimated by Scherrer's equation for various sintering temperatures, respectively. Figure 6 shows the TEM

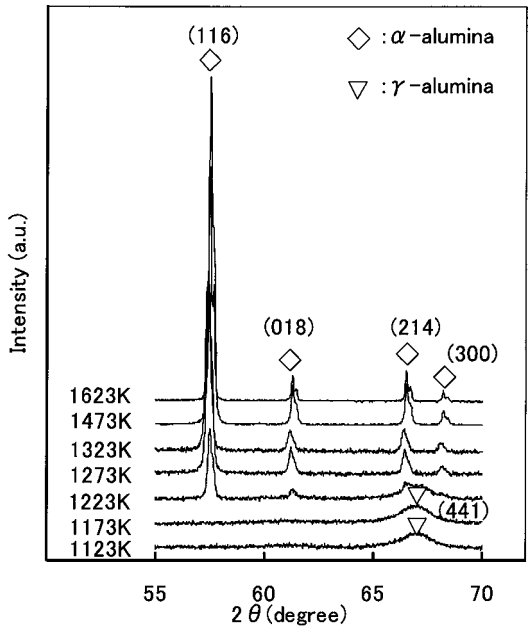


Figure 4 X-ray diffractions pattern of nano-structured Al_2O_3 as a function of sintering temperature. Initial particle size was 11.2 nm.

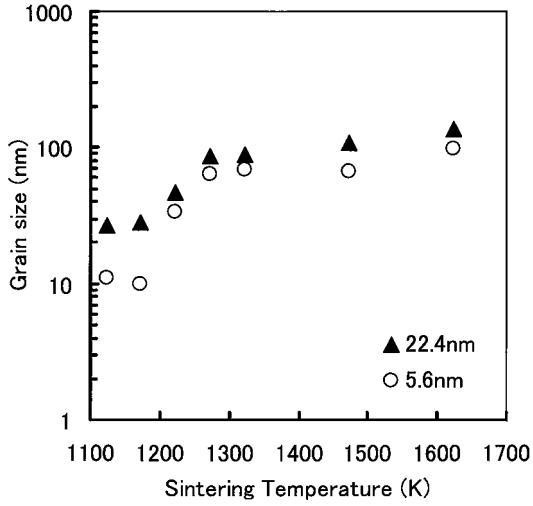


Figure 5 The sintering temperature dependence of grain sizes of nano-structured Al_2O_3 for various particles sizes.

photomicrographs of the samples sintered at (a) 1123 K, (b) 1273 K and (c) 1623 K and where the initial particle size was 5.6 nm and sintering time was 2 hours. As shown in Figs 5 and 6, there is a good agreement between the grain size estimated by Scherrer's equation from the XRD pattern and observed by TEM photomicrographs at under 1273 K. However, the results obtained at 1623 K were quite different. The particle size estimated by Scherrer's equation was 100 nm, the result of obtaining from the TEM photomicrograph exceeded 130 nm. The cause of this discrepancy was considered to be the internal stress according to quick phase transformation (from γ and α) and rapid crystal growth, when the grain rapidly grew at high temperature (1623 K). Thus this research was mainly discussed under 1323 K, because of having a good agreement between two measuring methods. The crystal phase of the sintered sample at below 1173 K was γ phase, and it was the same for the starting particle (Fig. 4.). In this temperature range, a grain growth was also not observed (Fig. 5.). However, the crystal phase had a sudden transformation from γ phase to α phase at 1223 K. This temperature was lowered by 250 K rather than a change of temperature of the crystal phases in bulk as reported by J. Freim *et al.* [15]. At the high temperature above 1223 K, the diffraction peak intensities of α phase was rapidly rising with increase of the sintering temperature. Also, the grain size rapidly grew approximately five times in the temperature range from 1123 K to 1323 K, and then it was slowly increased over 1323 K, as shown in Fig. 5. The TEM micrographs show the difference in grain growth of the samples sintered at 1123 K and 1273 K. These results suggest that there is a close relation between phase transformation and grain growth.

Figs 7–9 present the variation of the grain size of sintered samples at various particle sizes in starting power for various holding times at the sintering temperatures of 1123 K, 1173 K and 1273 K, respectively. In these figures, the (a) shows the grain sizes estimated by Scherrer's equation from XRD patterns, where the

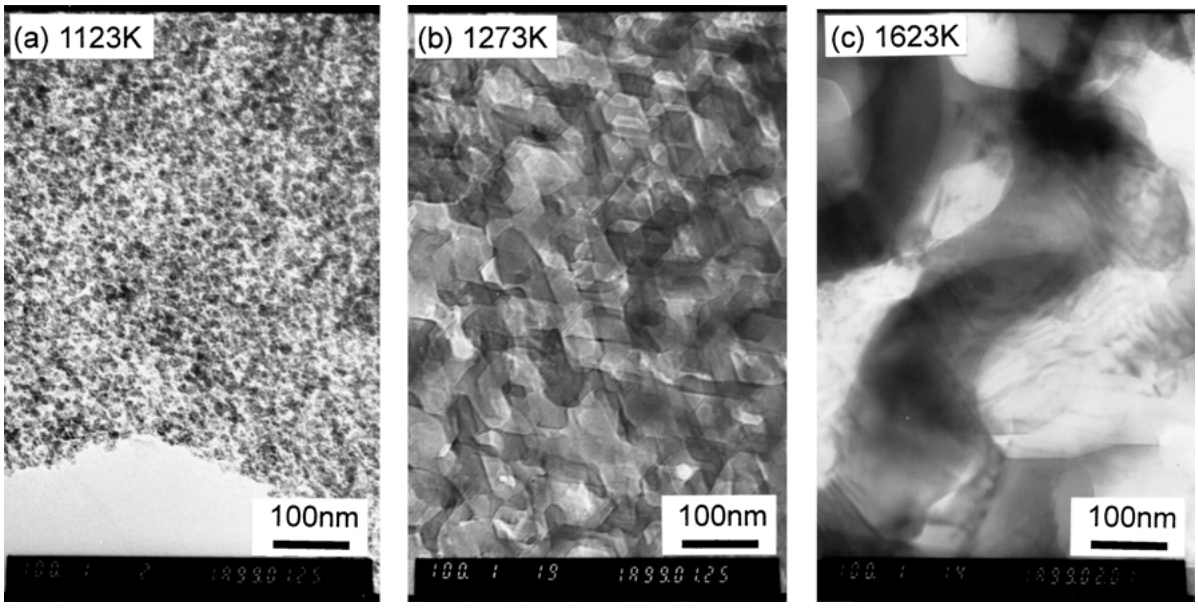
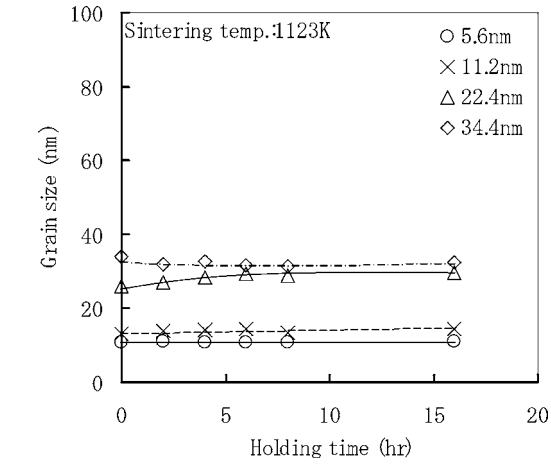
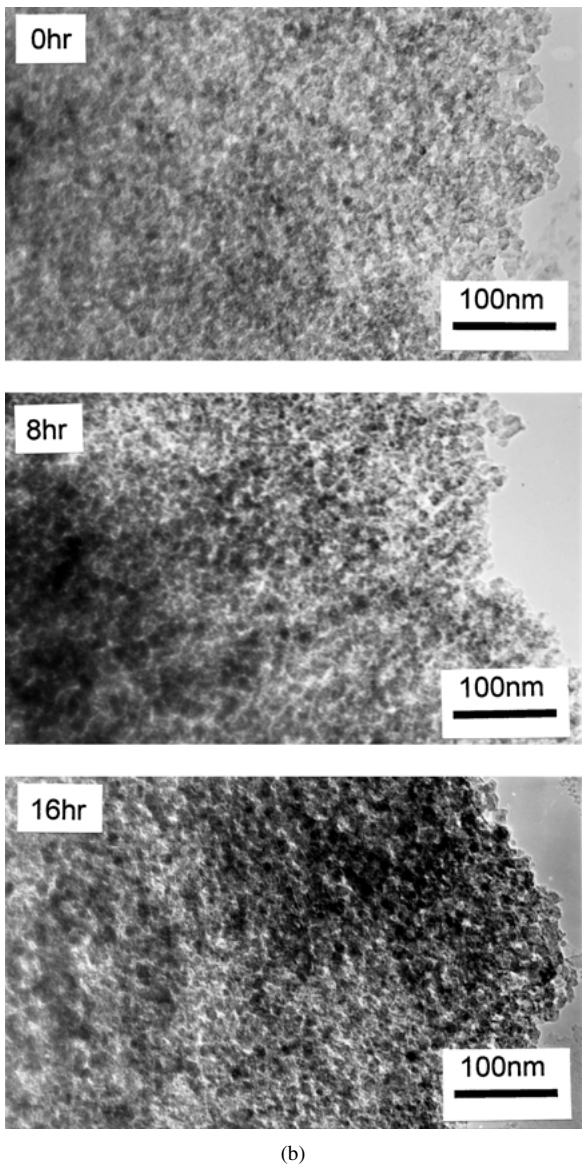


Figure 6 TEM micrographs of nano-structured alumina ceramics sintered at (a) 1123 K, (b) 1273 K, and (c) 1623 K.

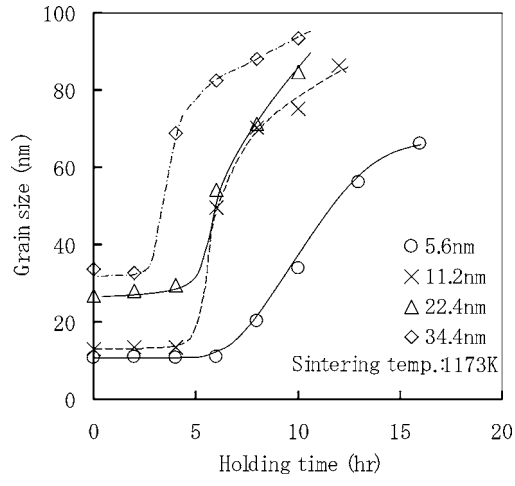


(a)

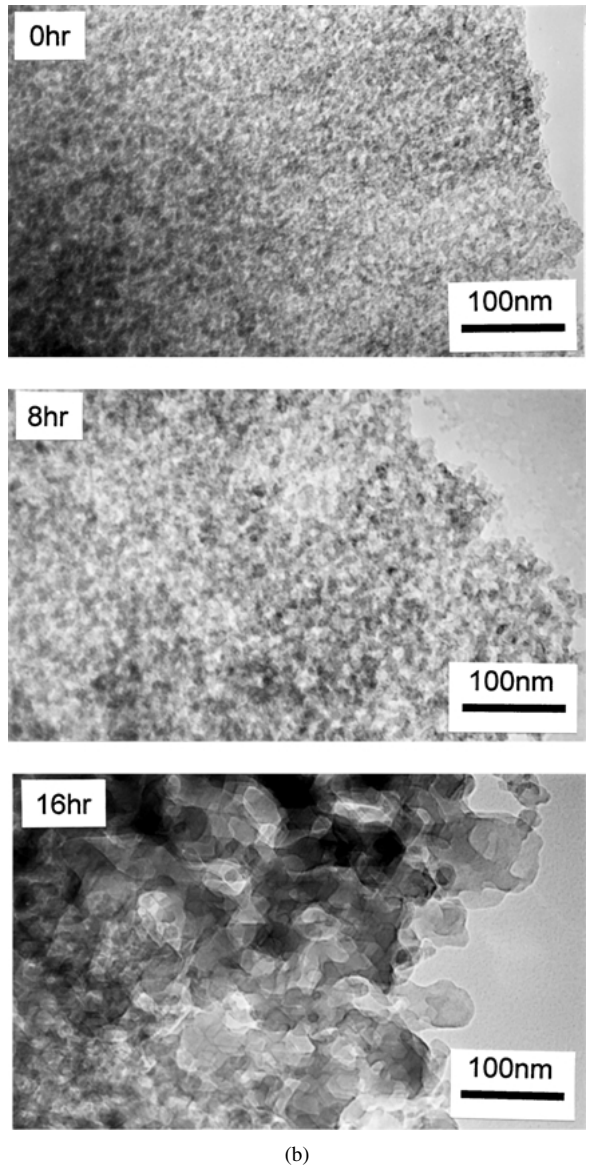


(b)

Figure 7 The grain sizes of nano-structured Al_2O_3 depending on initial particle size, sintering temperature and holding time at 1123 K.



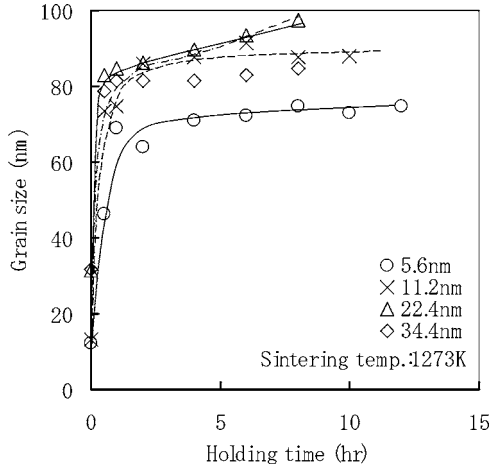
(a)



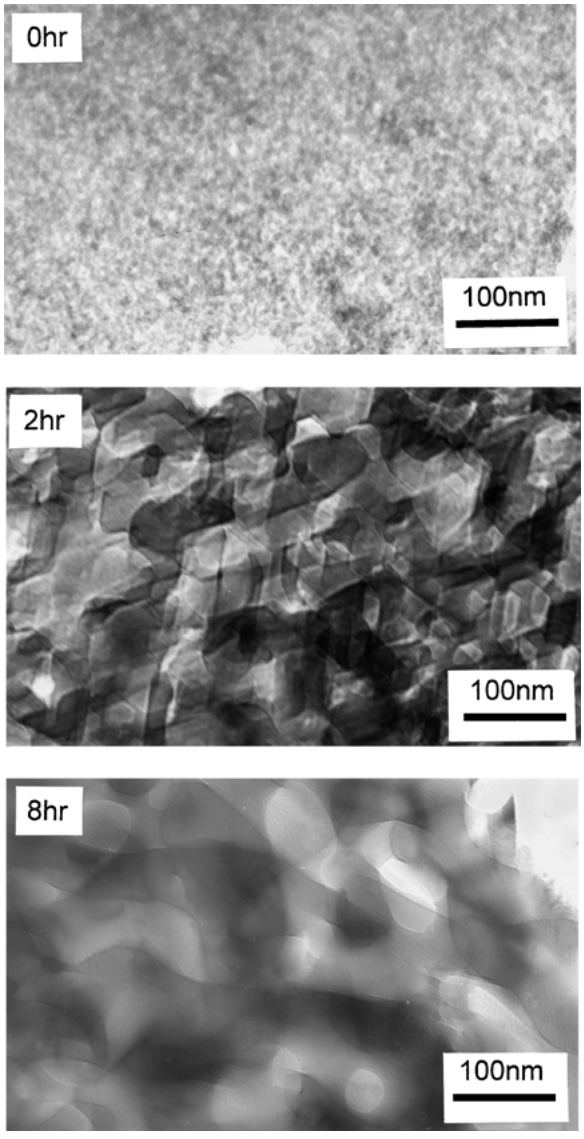
(b)

Figure 8 The grain sizes of nano-structured Al_2O_3 depending on initial particle size, sintering temperature and holding time at 1173 K.

vertical axis is the grain size and the horizontal axis is the holding time, and the (b) shows TEM microphotograph of the sintered sample with 5.6 nm. The pelletized samples were manufactured from nano-sized Al_2O_3 particles under the pressure of 2.5 GPa on a uniaxial direction for one minute. As indicated in Fig. 7, when the sintering temperature was 1123 K, the grain growth was not significant even though the holding time was more than 16 hours, and did not depend on the particle size. When the sintering temperature was 1173 K, the grain growth needed an incubation time as shown in Fig. 8. This incubation time was lengthened with



(a)



(b)

Figure 9 The grain sizes of nano-structured Al_2O_3 depending on initial particle size, sintering temperature and holding time at 1273 K.

decreasing particle sizes. After the incubation time, the grain growth rate rapidly increased. This rapid rate was particle size dependent, thus it decreased the smaller the particle size. As shown in Fig. 9, when the sintering temperature was 1273 K, the grain growth increased rapidly and directly without any incubation time, and then grain growth rate became quite low for a long holding time. The final grain size grew smaller by decreasing the particle size of the starting powder. From the XRD patterns and the TEM micrographs, the grain growth occurred mainly at the temperature of crystal phase transformation.

4. Conclusions

For nano-structured Al_2O_3 ceramics, nano-sized Al_2O_3 particles were synthesized by the MOCVD with $Al(CH_3)_3$. The crystal phases of the pelletized alumina samples prepared from the nano-sized Al_2O_3 particles dramatically transformed from γ-Al_2O_3 to α-Al_2O_3, when it was sintered above 1223 K for two hours. The temperature for the phase transformation of α-Al_2O_3 was lower by 250 K than a temperature of phase transformation in bulk. The grain sizes of nano-structured alumina ceramics increased as sintering temperature rise. The experimental results suggested that the grain growth needs an incubation time at the sintering temperature of 1173 K. This incubation time depends on particle size. After the incubation time, the grain growth rate increased rapidly. Above 1273 K, the grain growth directly occurred without any incubation time.

Finally, it is evident through this study that grain size control in nano-structured ceramics is strongly depended on the temperature of the phase transformation, and is improved when a sintering temperature has an incubation time.

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