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Examinations on the Critical and Primary Crystallite Sizes during θ- to α-Phase Transformation of Ultrafine Alumina Powders

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ABSTRACT

Examination on the existence of the critical and primary crystallite size ($d_c^{\alpha} \sim 17$ nm and $d_p = 50$–55 nm) phenomena during θ- to α-phase transformation of the nanosized Al_2O_3 powder was designed and conducted using two θ-Al_2O_3 powders of different crystallite sizes. Due to the critical size, the size dependence of the transformation temperature, the rate of transformation, and the inevitable presence of residual θ-phase in the thermal-treated and re-treated "100%-transformed" sample can be expected. Due to the two characteristic sizes and the formation of primary crystallites by the coalescence growth of the critical crystallites, the variation in mean α-size during the transformation can be predicted by means of the difference in the growth rate of the two θ-powder (different crystallite sizes) systems associated with proper thermal treatment techniques. Further, it is important to note that the presence of primary crystallites at various thermal-treated samples becomes possible.

1. Introduction. The phase transformation of θ- to α-Al_2O_3 is considered to occur through a nucleation and growth process.[1−3] Investigations on the critical crystallite sizes of transformation have been reported previously (Table 1),[4−24] although there is substantial discrepancy among them. Recent studies[25,26] on the nanosized alumina powder have found that during the transformation process there can be a critical size for θ-Al_2O_3 at the nucleation stage, which initiates the formation of the α-Al_2O_3 nucleus, and a primary size for the formed α-Al_2O_3 at the growth stage, beyond which the transformation comes to a completion. During the transformation process the size of θ-crystallites increased from 10 to about 22 nm (critical size, d_c^{θ}) (Scherrer formula−XRD)[27] and remained as monodispersed crystallites before its transformation to α-Al_2O_3. The α-Al_2O_3 nuclei thus formed showed a size of 17 nm (critical size, d_c^{α}), which grew up drastically to 50−55 nm (primary size, d_p) or larger before the polycrystalline α-Al_2O_3 particles were formed. Moreover, the formation of the α-Al_2O_3 nucleus was carried out from one θ-Al_2O_3 crystallite to one α-Al_2O_3 crystallite. And the primary crystallite was formed by coalescence of the α-nuclei.

The differential thermal analysis (DTA) curve of θ- to α-Al_2O_3 phase transformation generally shows an exothermic reaction at temperatures from near 900 to 1300 °C. The exothermic profile can be divided into two, lower ($T_n - T_b$) and higher ($T_b - T_p - T_o$) temperature components.[25] The

Table 1. Crystallite Sizes of θ- and α-Al_2O_3 Reported in Previous Studies

θ, nm	α, nm	methods	ref
small	500−1000	BET	4
20	30−40	XRD	5
70	>1000	XRD	6
20−30	100	TEM	7
	50	TEM	8
20	75−100	TEM	9
60	200−400	TEM, XRD	10
18.5	39.2	XRD	11
	90	BET	12
13	90	XRD	13
	30	BET	1
	54	BET, XRD	14
	<30	BET	15
	15.1	XRD	16
	70	BET	17
10	<60	BET, TEM	18
	15−200	TEM	19
	100	TEM	20
10−20	50−100	TEM, BET	21
	60−70	XRD	22
	50	XRD	23
	60	TEM	24

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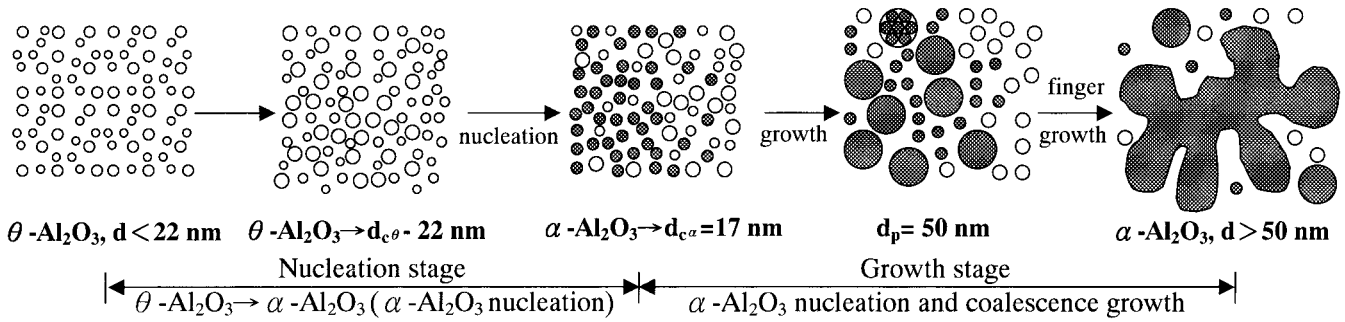

Figure 1. Schematic depiction of the growth phenomena of α-Al_2O_3 and α-Al_2O_3 crystallites as θ- to α-Al_2O_3 phase transformation.

former can extend to a wider temperature range, forming a broad and flat plateau that becomes manifest when the system is seeded with α-Al_2O_3.[28−31] The latter is sharp and strong. Meanwhile, the former can be obscure if a long time of isothermal heating at 1040 °C was employed.[32]

Studies[25,26] also indicated that the exothermic reaction is mainly related to the formation of α-nuclei and possibly slightly influenced by the growth of primary crystallites of the α-nuclei. This means that the nucleation process can occur throughout the temperature range and come into bloom at the peak stage. The temperature range covered by the DTA profile can be a function of the rate of α-Al_2O_3 formation: larger θ-Al_2O_3 crystallites that are closer to each other will narrow the temperature ranges.[26]

These studies provide the possibility of the existence of critical and primary crystallite sizes. Meanwhile, based on the variations in size measurements, the studies also inferred the necessity for θ-size growth and the coalescence mechanism for the growth of primary size. The whole crystallite growth procedure provided is shown in Figure 1: First the θ-crystallite is coarsening to the critical size, $d_c^{\theta} \sim 22$ nm for phase transformation, initiating the nucleation of α-nuclei with crystallite size $d_c^{\alpha} \sim 17$ nm. Then, secondarily, the formed α-nuclei coalesce to form primary crystallites with size $d_p \sim 50$ nm. And the driving force for the growth was also proposed by a traditional nucleation description[26,27] but attributed the presence of d_p to the arousing of the strain energy induced by the coalescence of d_c^{α} nuclei. However, the authors did not provide advanced observations to support the examinations. The direct investigation on the reaction between nanoparticles may encounter substantial difficulty, which makes the result obtained ineffective. However, there can be some other phenomena based on common logic of the growth mechanisms that will provide additional evidence.

The existence of a critical size phenomena during the transformation will initiate the problem of whether there will be a nanosized α-Al_2O_3 powder. This is because there are eventually θ-crystallites with sizes smaller than d_c^{θ}, which resulted from the fact that an insufficient number or mass of θ-crystallites to form the critical size during the stage of θ-growth will inevitably occur. And they will finally exist as the residual θ-crystallites in the 100%-transformed nanosized α-Al_2O_3 powder.

This study attempts to examine the certainty of existence of the critical and primary crystallite size phenomena during the θ- to α-Al_2O_3 phase transformation process. Experiments were designed and conducted using two θ-Al_2O_3 powders of different crystallite sizes based on conclusions drawn by previous studies.[24−26]

2. Experimental Section. (1) Design. *(a) Critical Crystallite Size.* (i) θ-Al_2O_3 crystallites with coarser sizes will phase transform at lower temperature. Due to the critical size, d_c^{θ}, for θ-Al_2O_3 crystallites to transform to α-Al_2O_3 nuclei of d_c^{α} and because there is no T_c point (phase transformation temperature) for the transformation,[33,34] the θ-size dependence of the transformation temperature and the rate of transformation can be expected. θ-Al_2O_3 powder samples with coarser crystallite sizes will attain the d_c^{θ} size faster during the heat treatment. Subsequently, it will be transformed to α-nuclei at lower temperatures. Or it will yield more α-nucleus formation than that of the samples with a smaller θ-size, if both get heat treatment at the same temperature.

(ii) Residual θ-Al_2O_3 crystallites are present in "100% phase-transformed" powders. Meanwhile, the presence of residual θ-phase in the thermal-treated and re-treated "100%-transformed" samples becomes inevitable. This is because the θ-crystallite in the transformation system is by no means identical in size and in intercrystallite distance. It is impossible that all θ-crystallites will reach the d_c^{θ} at the same time and transform to an α-nucleus at the same temperature simultaneously. Thus the existence of residual θ-crystallites with sizes smaller than d_c^{θ} will occur. Moreover, since the formation of the α-Al_2O_3 nucleus occurs from one θ- to one α-crystallite, it is apparent that the residual θ-crystallites can be impossible to connect with α-crystallites and transform to the α-phase. Thus a higher temperature and even several cycles of heat treatment become necessary for these θ-crystallites to reach the d_c^{θ} and then fulfill the phase transformation. These phenomena can be examined using DTA and TEM techniques.

(b) Primary Crystallite Size. It is obvious from previous studies[24,25] that, if there is a primary crystallite size, d_p, during the phase transformation, then the α-Al_2O_3 crystallite with this size will be the most abundant crystallite that can be found in the samples, accompanied with the critical one, d_c^{α}. Subsequently, the mean α-Al_2O_3 crystallite sizes measured by the XRD−Scherrer formula will be the [sum of d_c^{α}+ sum of d_p] divided by the total number of α-crystallites. Or the mean crystallite size of α-Al_2O_3, d_m is

$$d_m = (1 - x)d_c^{\alpha} + xd_p \quad (1)$$

Here x is the weight fraction of d_p-Al_2O_3. Since d_c^{α} and d_p are ~17 and ~50 (here 51 nm is used) nm, respectively, or 1 $d_p = 3\ d_c^{\alpha}$ (nm), and one crystallite of d_p is equivalent to 27 crystallites of d_c^{α} by weight, eq 1 can be expressed as

$$d_m = {}^1/_3 d_p + [x/(27 - 26x)]^2/_3 d_p \quad (2)$$

This means that $d_m = {}^1/_3 d_p = d_c$ when $x = 0$ and $d_m = d_p$ when $x = 1$. Further, the value of $[x/(27 - 26x)]$ (designated as y in Figure 2) when x ranges from 0 to 1 can be expressed as shown in Figure 2. It is noted that once the x value exceeds 0.7, a small increase in x would result in a big increase in y, which eventually brings about an increase in d_m. With reference to the thermal treatment conditions in relation to the amount of α-Al_2O_3 formation, and bearing in mind that the d_p-crystallite is formed by coalescence growth of d_c^{α}'s, it is obvious that, if the growth rate of d_c^{α} to d_p can be regulated, the variations of the α-size of the sample can be expected.

(i) Samples of smaller-sized θ-crystallites transform into samples of smaller-sized α-crystallites. It is familiar that compacts formed with finer particles will exhibit larger shrinkage during the initial stage of sintering.[27] α-Al_2O_3 crystallites transformed from finer-sized θ-Al_2O_3 crystallites will show similar effects, because they need more of the smaller θ-crystallites to form a d_c^{θ}. This offers a simple method to examine the variation of mean α-crystallite size as a function of the ratio of the two sizes, d_c^{α} and d_p. If proper techniques can be employed to restrain the growth rate of the formed d_c^{α}'s growing to d_p's, one will find that, for the same α-Al_2O_3 formation, the sample in which a higher amount of d_c^{α}-crystallite remained (smaller x in eq 2) will exhibit a smaller mean α-crystallite size. These phenomena can be examined using two θ-Al_2O_3 samples of different crystallite sizes. When the θ-crystallite approaches the d_c^{θ} size and transforms to α-nuclei, the sample of smaller size will shrink more. This indicates that the interparticle distance between each formed α-nucleus is larger, and a higher driving force is required for the following formation of the primary crystallite. Relating the amount of formation with the mean crystallite size of α-Al_2O_3, the size obtained from samples of smaller-sized θ-crystallites will be smaller.

(ii) α-Crystallites obtained from samples of larger-sized θ-crystallites exhibit sizes close to d_p. Similarly, since the interparticle distance between each formed α-nucleus of samples obtained from larger-sized θ-crystallites will be smaller and eventually it will be easier for the nuclei to coalesce, forming d_p-α-Al_2O_3 (higher x value), the α-sizes obtained from samples of larger θ-crystallites exhibit sizes close to d_p.

(2) Sample Preparation. *(a) Preparation of θ-Al_2O_3.* θ-Al_2O_3 powders of two crystallite sizes, 22 and 25 nm (XRD-Scherrer formula, Designed as S2 and S5, respectively) were used in preparing samples for this study. The S2 was prepared by calcination of boehmite gels (Remet Chemical Corp.). The boehmite was diluted in DI water and treated by mechanical dispersion using ultrasonic waves (Misonix XL2020 Ultrasonic Liquid Processor, 20 kHz, 300 W) for 8 min. Most of the water then was removed by spray drying. The as-received xerogel was oven-dried at 80 °C for 24 h and then calcined in air at 960 °C for 64 h[35] to obtain θ-Al_2O_3 powders with a mean crystallite size of 22 nm (Scherrer formula) (Table 2). Another θ-Al_2O_3 powder, S5, of larger mean crystallite size (25 nm) was purchased directly from market (Ceralox Co.).

Table 2. Basic Properties of the Starting θ-Al_2O_3 Powders

sample no.	phase	θ-crystallite diameter (nm)[a]	BET surface area (m^2/g)
S2	θ(δ)	22	68
S5	θ(δ), α[b]	25	45

	chemical analysis (ppm)					
	SiO_2	Fe_2O_3	CaO	MgO	Na_2O	S
S2	tr	tr	tr	tr	tr	tr
S5	<4	128	2	28	nd	nd

[a] XRD−Scherrer formula. [b] Less than 3.5 wt %.

(b) Preparation of Observing Samples. To attain samples for observing the phase transformation process, thermal treatments through the quench technique were conducted for the θ-Al_2O_3 powders, to freeze the phase transformation process at specific temperatures. Both S2 and S5 were examined by differential thermal analysis (DTA, Netzsch STA409, using ignited alumina as the reference material) and thermal dilatometry (DIL, Netzsch DIL402) in advance. A heating rate of 10 °C/min was used. Samples for observation were then obtained by isothermal annealing at scheduled temperatures referred to in the DTA profiles. The furnace was first brought to the scheduled temperature and then the θ-Al_2O_3 powders, which were placed in platinum crucibles, were loaded. About 20 s was required to restabilize the furnace temperature after the crucible was loaded. Quenching was performed with a cooling rate of >500 °C/min. All data present in the study are mean values of three samples.

(3) Powder Characterization. The crystalline phase was identified by XRD (Rigaku, D/MAX B) powder methods using Ni-filtered Cu Kα radiation, $2\theta = 20-80°$. XRD powder methods were also employed to determine α-Al_2O_3 formation using CaF_2 as the internal standard. The calibration line was established by calculating area ratios between α-Al_2O_3 (012) and CaF_2 (111) measured from a series of θ-Al_2O_3 samples in which varying ratios of α-Al_2O_3 and 10 wt % CaF_2 were formulated.

The mean crystallite sizes of θ- and α-Al_2O_3 of the powders were determined by the XRD−Scherrer formula (mean crystallite size $= 0.9\lambda/(B \cos\theta)$, where $\lambda = 1.540\,562$ Å, B is the broadening of the full width at half-maximum (fwhm) peak height in radians, and θ is the Bragg angle). It was applied to peaks (012) and $(20\bar{2})$ of α- and θ-Al_2O_3, respectively. The instrument peak width calibration was obtained using a well-crystallized α-Al_2O_3 powder. The

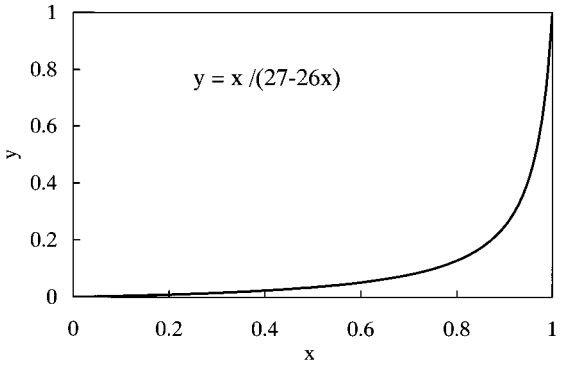

Figure 2. Plot for $y = x/(27 - 26x)$ as x ranges from 0 to 1.

calculation was assisted by a software, XRD Pattern Processing and Identification, Jade for Windows, Version 3.0, developed by Material Data Inc. The conventional nitrogen absorption technique (BET) (Micromeritics, Gemini 2360) was adopted to measure the specific surface area of the observing samples, by which the surface area diameter of the sample was evaluated.

Residual θ-Al_2O_3 phase present in the transformation systems was examined by DTA (DTA, Netzsch STA409) with heating rates of 10 and 15 °C/min, using ignited alumina as the reference material. The transmission electron microscopic techniques (TEM, Hitachi HF-2000 field emission transmission electron microscope) were also employed to examine the morphology and the microstructure of the residual θ-Al_2O_3 particles present in the transformation systems. Measurements for thermal expansion of S2 and S5 powders were obtained by a dilatometer (Netzsch, DIL 402).

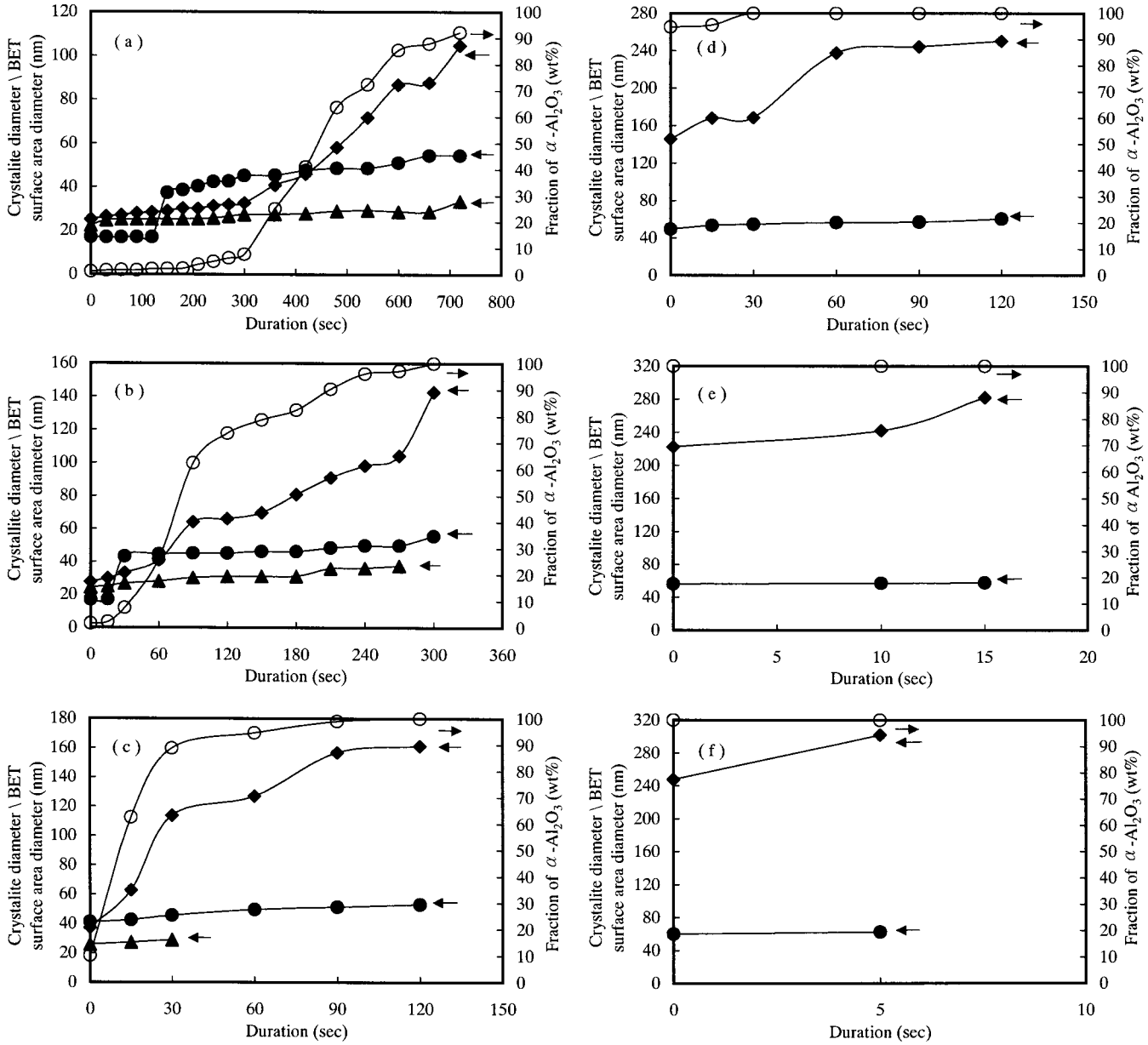

Figure 3. Relationships between the fraction of α-Al_2O_3 phase formation and the size variations of θ- and α-Al_2O_3 crystallites and BET diameter during θ- to α-phase transformation of S2 powders. Samples were annealed at (a) 1190, (b) 1240, (c) 1280, (d) 1330, (e) 1380, and (f) 1430 °C for varying times. Key: (●) crystallite size of α-Al_2O_3; (▲) crystallite size of θ-Al_2O_3; (♦) BET surface area diameter; (○) fraction of α-Al_2O_3 formation.

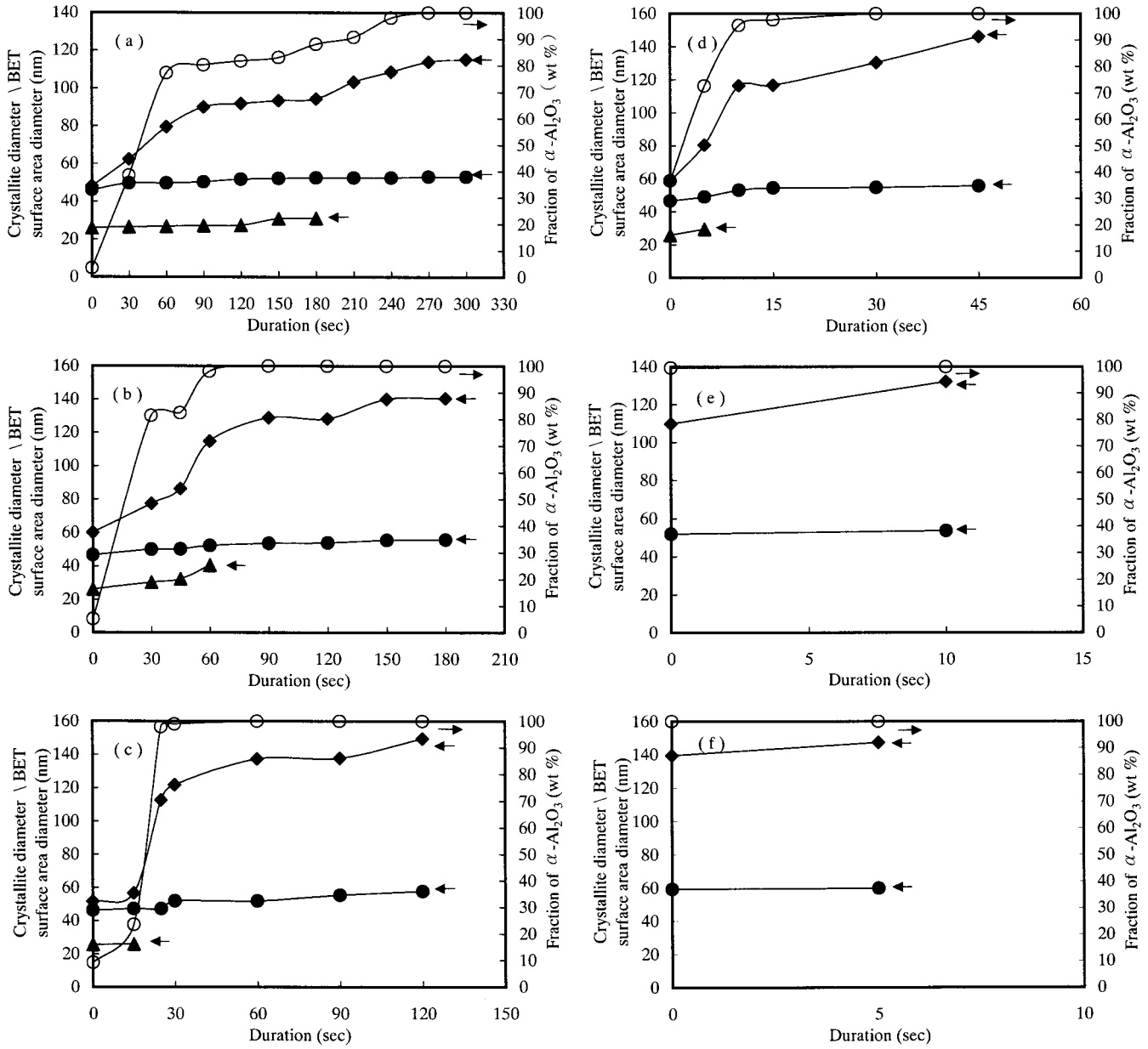

Figure 4. Relationships between the fraction of α-Al_2O_3 phase formation and the size variations of θ- and α-Al_2O_3 crystallites and BET diameter during θ to α-phase transformation of S5 powders. Samples were annealed at (a) 1190, (b) 1240, (c) 1280, (d) 1330, (e) 1380, and (f) 1430 °C for varying times. Key: (●) crystallite size of α-Al_2O_3; (▲) crystallite size of θ-Al_2O_3; (♦) BET surface area diameter; (○) fraction of α-Al_2O_3 formation.

Both powder samples were isostatically pressed (100 MPa) into compacts to limit the density difference (bulk density 1.5 g/cm^3).

3. Results and Discussion. (1) Crystallite Size, BET Diameter, and α-Al_2O_3 Formation. Figures 3 and 4 demonstrate the relationships among the α-Al_2O_3 phase formation and the crystallite and BET sizes of θ- and α-Al_2O_3 during θ- to α-phase transformation of the two θ-Al_2O_3 powder systems. The phase transformation was preceded by heat treatments at 1190−1430 °C for varying durations (in seconds). In general, the α-Al_2O_3 formation and the growth of θ- and α-Al_2O_3 crystallite sizes are identical to those described previously.[25,26] The θ-Al_2O_3 crystallite sizes remained in a narrow range of 20 to ∼30 nm. And α-sizes were about 17 nm on appearance and then coarsened to 40−50 nm abruptly without having a proper proportional increase in α-Al_2O_3 formation. Meanwhile, it is found that, at the lower temperature range of 1190−1280 °C, the amount of α-Al_2O_3 formed in finer-θ-sized S2 samples was less than that formed in coarser S5 samples, if the same holding time was employed. Raising the treatment temperatures eventually reduced the difference. Similar results were revealed by XRD examinations (Figure 5). It demonstrates that the closeness of larger θ-crystallite size to d_c^θ needs a relatively smaller amount of energy for the growth to d_c^θ and the following nucleation of the α-phase. Raising treatment temperatures

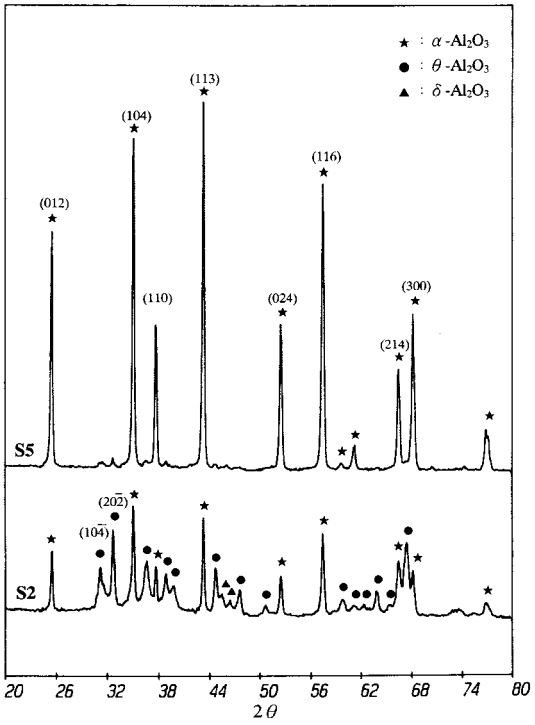

Figure 5. Typical XRD patterns of S2 and S5. Both sample were thermal-treated at 1240 °C for 60 s.

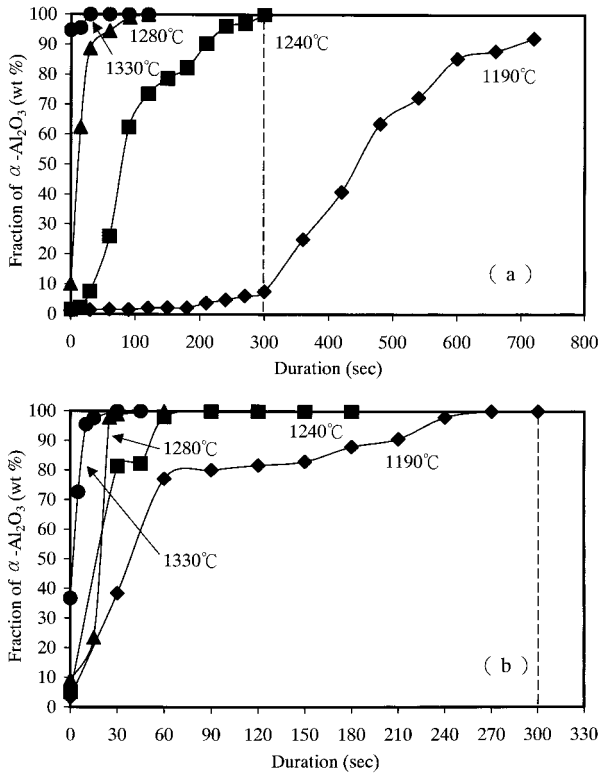

Figure 6. Relationships between the annealed time and fraction of α-Al_2O_3 formation of S2 (a) and S5 (b) samples.

can also accelerate the growth of a smaller θ-crystallite (S2) to the d_c^{θ} size and eventually reduces the difference of α-Al_2O_3 formation between S2 and S5 samples.

(2) Critical Crystallite Size. *(a) θ-Al_2O_3 with coarser crystallite sizes will phase transform at lower temperatures.* Figure 6 illustrates the difference of α-Al_2O_3 formation during the phase transformation between S2 and S5 samples treated under identical thermal conditions. Obviously, due to the existence of the critical size, d_c^{θ}, and because there is no T_c point, the θ-size dependence of both the transformation temperature and the α-formation can be properly reflected by the size differences. For S2 samples, since the θ-size was smaller, the growth period of d_c^{θ} for samples treated at 1190 and 1240 °C was observed, compared to that of the S5 sample with the same temperature, by the time intervals of 300 and 30 s, respectively, before the blooming of α-Al_2O_3 crystallite formation. This is attributed to the fact that the coarser θ-crystallites in sample S5 would attain the d_c^{θ} easier; hence it transformed to α-nuclei at lower temperatures, resulting in the higher yield of α-formation at the same temperature, compared to that of the finer-θ-sized S2 samples.

(b) Residual θ-Al_2O_3 crystallites appear in "100% phase-transformed" powders. The presence of residual θ-phase in the thermal-treated and re-treated "100%-transformed" samples can be observed using DTA techniques. Figure 7 shows the DTA profiles of one heat-treated S5 sample with four repeat DTA measurement. The sample was first heated to 1300 °C (heating rate 10 °C/min), comparable to the time needed to finish a DTA measurement cycle, and then subsequently re-experienced a total number of four DTA measurements. It is impressive to find that at the first measurement, there was an exothermic peak (T_p), indicating that a considerable amount of θ- to α-phase transformation occurred as usual. However, it is noted that there can be another exothermic reaction appearing at ~1400 °C. Repeating the DTA measurements for the same sample revealed that there can be two exothermic reactions on the profiles, $I_{x1,2,3,...}$ and $T_{p1,2,3,...}$ (Figure 7a) instead of the ordinary exothermic reaction, T_p, illustrating that there was transformation occurring in sequence. And, possibly, the transformation for some of the θ-crystallites can only occur at temperatures higher than that generally occurs. Further, since the heat treatment can result in the growth of the α-Al_2O_3 crystallites as well (Figures 2 and 3), the θ-growth may thus be hindered by the neighboring α-Al_2O_3 crystallites. The hindrance becomes more serious, as the heat treatment is repeated, resulting in the raising of transformation temperatures by about 200 °C (Figure 7, T_{p1}, etc.). It is also noted that the height of the exothermic peak and the peak temperature was lowering as well as going higher gradually, with an increase in the number of reheating cycles. Both phenomena can be expected because of the decrease in transformation quantity and the deterioration in diffusion conditions for the residual θ-crystallites. Thus it is obvious that there are residual θ-crystallites present in the nanosized high-purity α-Al_2O_3 powders, but it may be an extremely small amount. And, it will be mentioned that the reaction between α- and θ-Al_2O_3 crystallites may not occur. Figure 8 shows two typical θ-Al_2O_3 crystallites present in α-Al_2O_3 systems. In Figure 8a, a θ-crystallite of ~25 nm is neighbor to α-crystallites of

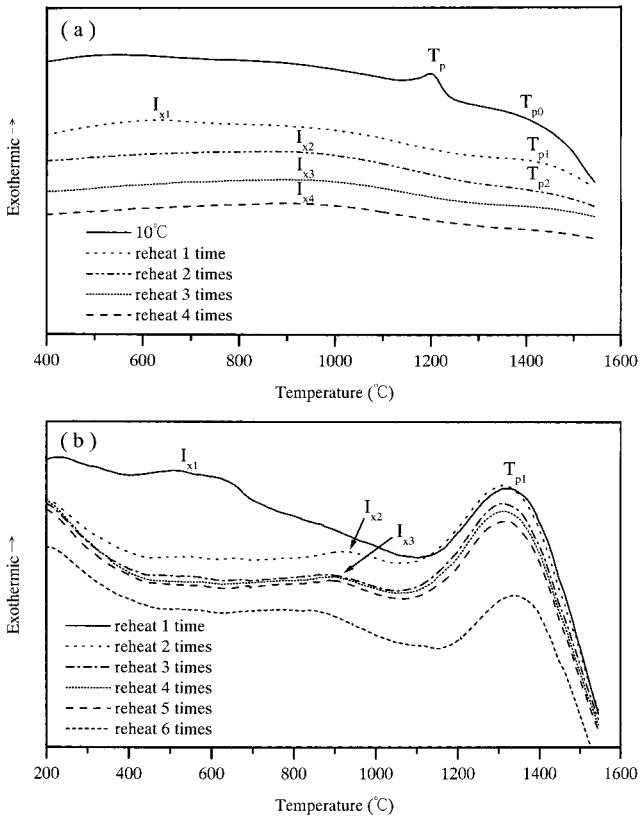

Figure 7. Typical DTA profiles showing an inevitable presence of residual θ-Al_2O_3 crystallites in α-Al_2O_3 powders. S5 samples with 10 °C/min (a) and 15 °C/min (b) heating rates.

>100 nm. And in Figure 8b a θ-crystallite of similar size is enclosed by α-crystallites of >100 nm with finger growth.[36]

(3) Primary Crystallite Size. *(a) Samples of smaller-sized θ-crystallites transform into samples of smaller-sized α-crystallites.* Figure 9 confirms that the finer-sized θ-Al_2O_3 powder will exhibit a higher thermal shrinkage during the θ- to α-phase transformation. On the basis of this, the formed d_c^{θ}-θ-crystallites and the subsequently occurring α-Al_2O_3 nuclei in the S2 samples would be at a longer distance from each other, compared to that of the S5 samples. And it eventually gave rise to a need of higher driving force for the coalescence growth of the d_p-crystallite. Figure 10 organizes the α-crystallite size variation vs the fraction of α-formation of all the samples of S2 and S5 after heat treatments. All samples were prepared by fast-rate-heating and quenching techniques so as to restrain the growth rate of the formed d_c^{α}'s growing to d_p's. A size difference of 5 nm at a lower fraction (0−10%) of α-formation and above 10 nm at a higher fraction (50−90%) of α-formation was observed. Since α-Al_2O_3 nuclei transformed from finer-sized θ-Al_2O_3, crystallites will separate farther and eventually result in a higher ratio of number of d_c^{α}-crystallites to number of d_p-crystallites. The smaller mean α-crystallite size exhibited by S2 samples compared to that of S5 is manifested.

(b) α-Crystallites obtained from samples of larger-sized θ-crystallites exhibit sizes close to d_p. Similarly, since the interparticle distance between each formed α-nucleus of samples obtained from larger-sized θ-crystallites, S5, were smaller and eventually it was easier for the nuclei to coalesce forming d_p-α-Al_2O_3, the α-sizes obtained from samples S5 exhibited sizes close to d_p. Figure 11 shows that at the same amount of α-Al_2O_3 formation, the mean α-size measured for a specific temperature of the S2 samples was smaller than that of the S5 samples. Further, the size deviation from size d_p for the specific temperature of samples S2 was larger. And the deviation increased with the raising of temperature (Figure 11a). Both are attributed to the fact that there are two simple crystallite sizes, d_c^{α} and d_p, present in the transformation system. The distance among the critical

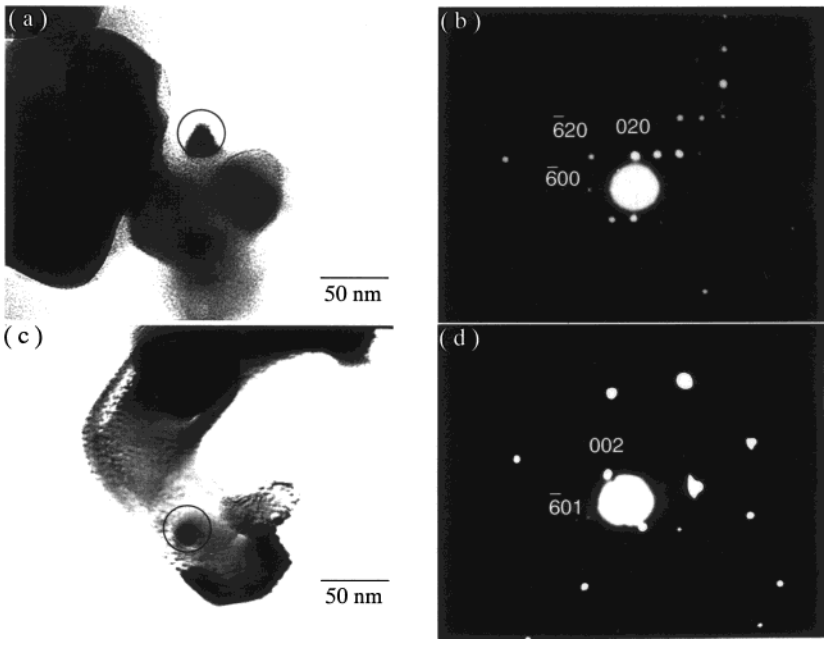

Figure 8. Typical α-Al_2O_3 crystallites present in "high-purity" α-Ala-Al_2O_3 powders: θ-crystallite of ~25 nm neighboring α-crystallites of >100 nm (a) and enclosed by α-crystallites of >100 nm with finger growth (b).

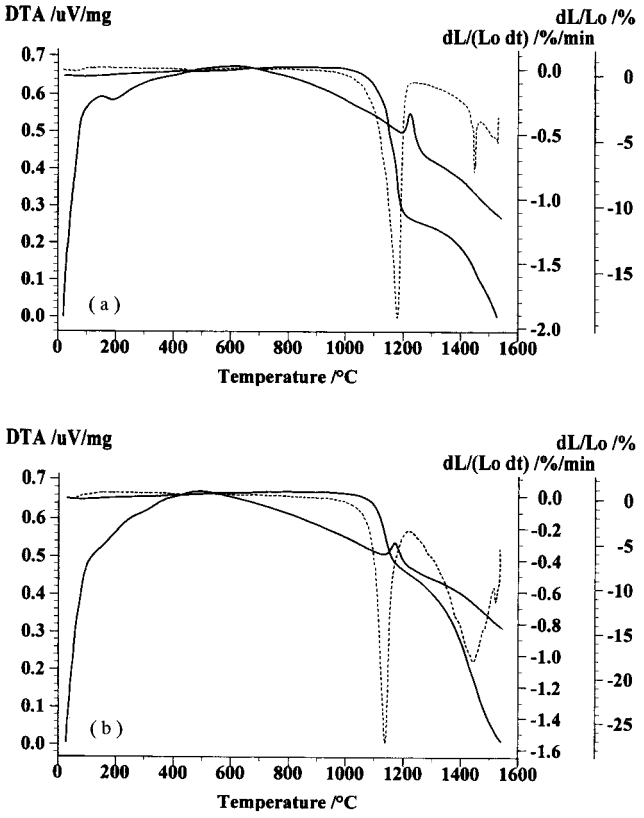

Figure 9. Samples of coarser-sized θ-crystallites (b), compared with finer-sized (a), exhibited lower thermal shrinkage, indicating the easier nucleation and growth stages of θ- to α-phase transformation.

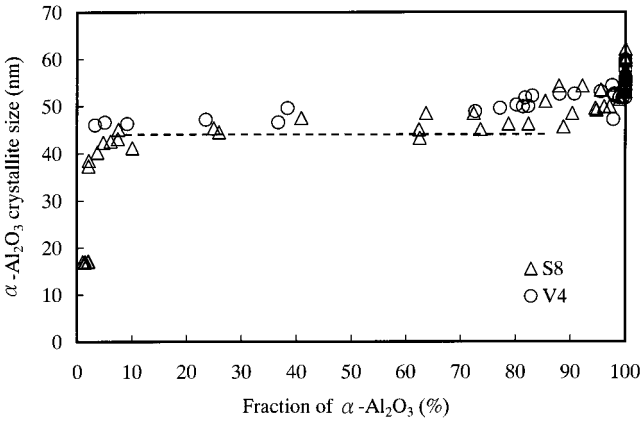

Figure 10. Samples of smaller-sized θ-crystallites transformed into samples of smaller-sized α-crystallites.

crystallites will determine the accessibility of the primary crystallite formation. The subsequent decrease in the larger number of d_c^{α} to form, if it occurs and will occur easily for S5 samples, smaller numbers of d_p-Al_2O_3 will induce a substantial closeness of the mean α-Al_2O_3 size to the primary one. The size difference between temperatures 1190 and 1240 °C for samples S2 and S5 are 5 and 2.5 deg, respectively, and the mean α-sizes of S5 samples were closer to d_p (50 nm) (Figure 11a,b); both are attributed to and are in accordance with the fact that there exist critical and primary

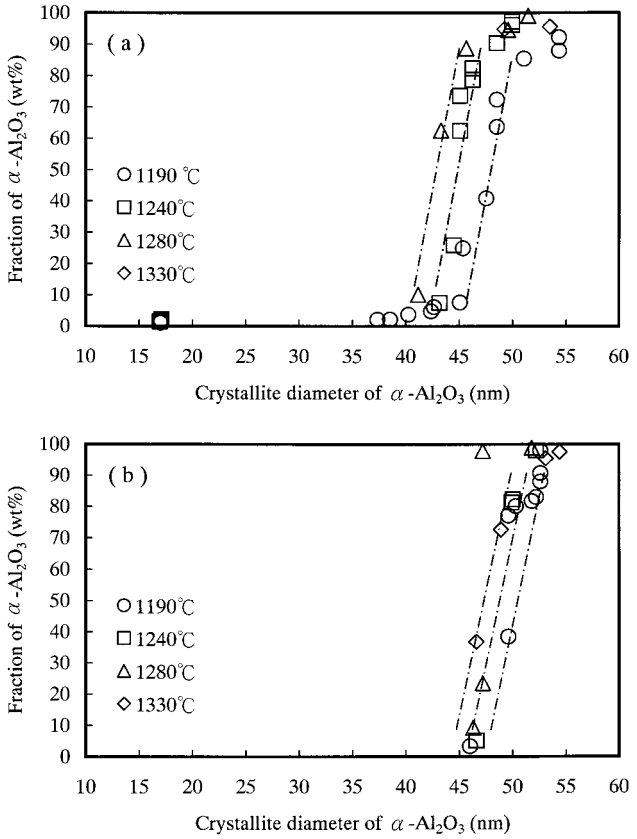

Figure 11. Fine-sized S2 (a) shows wider mean α-crystallite size distribution spectra with respect to annealing temperatures, compared to that of the coarse-sized S5 (b).

crystallite sizes for the nanosized Al_2O_3 powder during the θ- to α-phase transformation.

4. Conclusions. The existence of critical and primary crystallite sizes during θ- to α-phase transformation of nanosized Al_2O_3 powders was proved by using two θ-Al_2O_3 powders of different crystallite sizes.

Due to the existence of the critical size and no T_c point for θ-crystallites to transform to α-nuclei, samples with coarser θ-crystallite sizes will experience phase transformation at lower temperatures. And it will eventually yield more α-nucleus formation at the same temperatures, compared to that of the smaller θ-crystallite samples.

Meanwhile, the presence of residual θ-phase, which could not reach the critical size in the thermal treatment, becomes inevitable. Thus, for the residual θ-Al_2O_3 crystallites, a higher temperature and even several cycles or longer duration of heat treatment become necessary for the fulfillment of the phase transformation.

Since there is a primary crystallite size during the phase transformation, it leads to the fact that the most common diameter for the crystallites found in the samples is primary size. Subsequently, when the coalescence growth rate of the primary crystallite formation is restrained, the mean α-Al_2O_3 crystallite sizes obtained then fully reflect the number ratio between the primary and critical crystallites. Samples of smaller-sized θ-crystallites transform into samples with

smaller mean α-crystallite sizes. And, the mean α-crystallites diameter obtained from samples of larger θ-size will be closer to primary size.

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