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Thermal analysis of phase transformation kinetics in α-Al_2O_3 seeded boehmite and γ-Al_2O_3

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Abstract

The effect of α-Al_2O_3 seeding on the transformation kinetics of high purity commercial boehmite and γ-Al_2O_3 was investigated. The effect of seed size, powder purity, sample homogeneity, and sample density on the transformation kinetics are discussed. The temperature and activation energy of the θ to α-Al_2O_3 phase transformation decreases for boehmite and γ-Al_2O_3 powders with an appropriate addition of α-Al_2O_3 seed particles. For 5 wt.% seeded (2×10^{15} seeds/cm^3 γ-Al_2O_3) boehmite samples, the transformation temperature and activation energy were decreased by 85°C and 115 kJ/mol, respectively, compared to unseeded boehmite. For 5 wt.% seeded γ-Al_2O_3 samples, the transformation temperature and activation energy were decreased by 75°C and 170 kJ/mol, respectively, compared to unseeded γ-Al_2O_3. © 1998 Elsevier Science B.V.

Keywords: Thermal analysis; Activation energy; Phase transformation; Alumina; Seeding

1. Introduction

Transition alumina powders are intrinsically nanocrystalline and can be synthesized from a variety of precursors. The most common precursors for α-Al_2O_3 are boehmite (γ-AlOOH) and γ-Al_2O_3. Boehmite, and the less ordered 'pseudoboehmite' are aluminum hydroxides, which decompose to form polycrystalline γ-Al_2O_3 upon heating above 450°C [1]. Upon heating, γ-Al_2O_3 undergoes a series of polymorphic phase transformations from a highly disordered cubic close packed lattice to the more ordered cubic close packed θ-Al_2O_3. When heated to ≈1200°C, θ-Al_2O_3 undergoes a reconstructive transformation by nucleation and growth, where the oxygen atoms rearrange into a hexagonal close packed structure to form thermodynamically stable α-Al_2O_3[2].

A large number of investigators have attempted to control the kinetics and microstructural evolution of the θ to α-Al_2O_3 phase transformation with the addition of small amounts of metal oxide seed particles [3–19]. In unseeded boehmite, the intrinsic nucleation density is 10^8–10^{11} nuclei/cm^3 γ-Al_2O_3 and ≈1200°C is required to fully transform the material to α-Al_2O_3 in 100 min [3,8,10,13,20,21]. The addition of seeds, which are isostructural with α-Al_2O_3, provide low energy sites for heterogeneous nucleation and thus reduce the activation energy barrier required for transformation, and the transformation temperature [4,5].

A plot of the θ to α-Al_2O_3 phase transformation temperature as a function of seed concentration for

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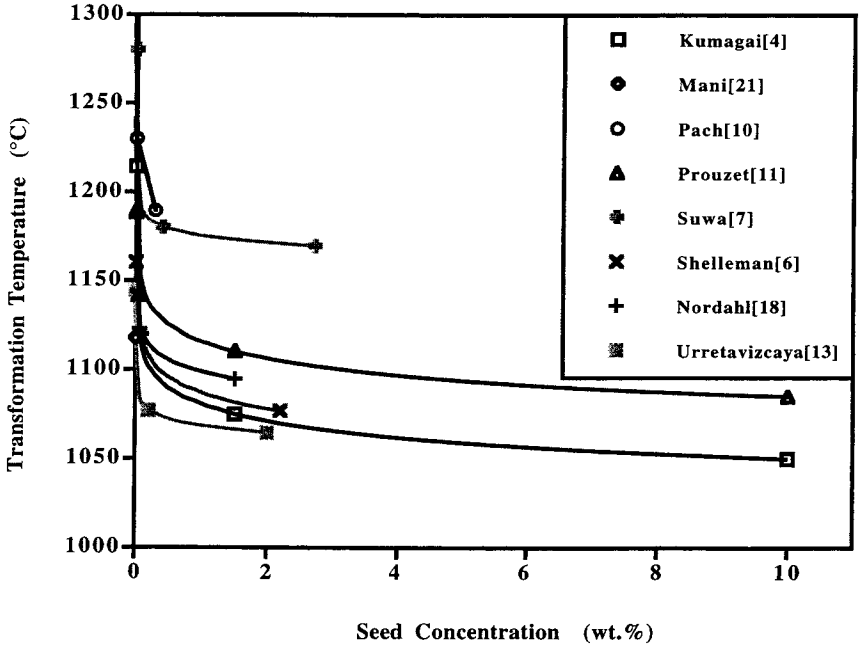

Fig. 1. θ to α-Al_2O_3 phase transformation temperatures for α-Al_2O_3 seeded boehmite and transition alumina as a function of wt.% seeds.

various investigations of α-Al_2O_3 seeded transition alumina is shown in Fig. 1. In these studies, unseeded boehmite transforms at 1120–1280°C, depending on the purity and particle size of the boehmite. The transformation temperature decreases rapidly with seed concentration ≤2 wt.%, then tapers off at higher seed concentrations. Kumagai and Messing lowered the transformation temperature by 140°C with 1.5 wt% seed concentration [5] while, other investigators observed temperature decreases of 110°C, 85°C, 80°C, and 40°C for 2.7, 2.0, 1.5 and 0.3 wt.% additions, respectively [7,13,11,10]. In the case of seeded boehmite-derived γ-Al_2O_3, Shelleman and Messing lowered the transformation temperature by 83°C with 2.2 wt.% seed addition [6] whereas, Nordahl and Messing lowered the transformation by 90°C with 1.5 wt.% seed addition [18]. The decreasing transformation temperature behavior was consistent for all of the materials investigated. The variability of the transformation temperature is most likely due to differences in the impurity content, seed size, and degree of sample homogeneity.

A plot of the θ to α-Al_2O_3 phase transformation temperature for seeded transition aluminas for other metal oxide seeds is shown in Fig. 2 [7,9,12,14]. For the unseeded systems, the transformation temperature ranges from 1215°C to 1280°C. The oxides shown to have an effect on nucleating the phase transformation, in order of magnitude, were Fe_2O_3, CuO/Cu_2O, TiO_2, V_2O_5, and $MgAl_2O_4$. Cr_2O_3, SiO_2, and ZrO_2 had conflicting effects; lowering the transformation temperature in one investigation and raising it in another. B_2O_3, La_2O_3, Y_2O_3, and CaO all impeded the phase transformation and increased the transformation temperature relative to unseeded samples. Ta_2O_5, Li_2O, and MgO did not affect the transformation temperature. Although, the magnitude of the transformation temperature varies between the investigations, it is evident that Fe, Cu, and Ti oxides are effective in nucleating the phase transformation [7,9,12,14,22,23]. In addition, the use of salt addition, which presumably produce fine precipitate seeds is more effective in reducing the transformation temperature than adding larger seed particles [9]. In this manner, significantly higher seed concentration can be produced in situ during precipitation.

A conventional approach to study transformation kinetics is to carry out an Arrhenius analysis at a series of isothermal temperatures and quantitative X-ray analysis of phase development. In this case, many

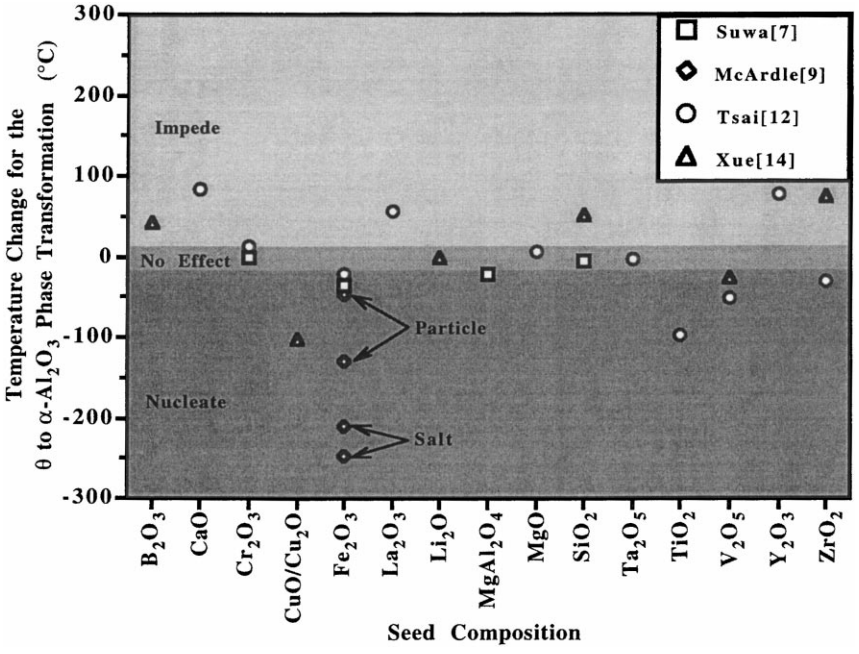

Fig. 2. Change in the θ to α-Al_2O_3 phase transformation temperature for various metal oxide seeds.

samples are needed to obtain an accurate activation energy for the transformation. An alternative method to obtain the activation energy for the θ to α-Al_2O_3 phase transformation was developed in 1956 by Kissinger [24]. The Kissinger analysis requires only the peak temperature of the phase transformation at various heating rates.

Several investigators have reported activation energies for the θ to α-Al_2O_3 phase transformation in unseeded boehmite and transition aluminas under isothermal conditions. Activation energies of 431–600 kJ/mol were obtained by X-ray analysis of isothermally heated samples [13,25–27]. For methods based on differential thermal analysis, activation energies ranged from 670 to 850 kJ/mol for integration techniques [28–30] and was 600 kJ/mol using the Kissinger analysis [31].

Schaper and Van Reijen investigated the transformation kinetics of γ-Al_2O_3 by differential thermal analysis (DTA) [31]. Twenty DTA curves were obtained at a constant heating rates between 4 and 40°C/min and the data were analyzed by a variety of techniques. The techniques and corresponding kinetics parameters utilized are listed in Table 1 [31]. For the same set of data, the activation energies ranges from 600 to 850 kJ/mol, but the order of the reaction, n, was ≈1 in all cases. The first three methods listed in Table 1 are based on the values of dx/dt and x, where x is the fraction of α-Al_2O_3. The variability in data and the lack of consensus about which approach is best suited for analysis of the α-Al_2O_3 transformation led us to select the Kissinger approach for analysis. It should be noted that the Kissinger derivation assumes the following [24]:

1. The temperature of the thermocouple is the temperature of the entire sample.
2. The peak maximum of the DTA peak represents the temperature of the maximum reaction rate. Modern thermal analysis equipment assures that 1 and 2 are true.
3. The heat capacity of the holder and material remains constant throughout the run. For small sample sizes i.e. 25 mg, the temperature change during the exothermic peak is ≤3°C, therefore, the change in heat capacities for the rapid, but nominal, temperature change is assumed to be negligible.
4. The reaction is first order. Due to the consistency of reaction orders obtained by the various analysis techniques given in Table 1, it is assumed that the

Table 1
Differential thermal analysis methods for determining kinetic parameters of the θ to α-Al_2O_3 phase transformation in γ-Al_2O_3

Method	*x*-axis	*y*-axis	Activation energy (kJ/mol)	Reaction order (n)
Borchardt and Daniels [28]	T^{-1}	$\ln\left[\frac{(dx/dt)}{(1-x)^n}\right]$	670	1
Freeman and Carroll [29][a]	$\frac{T_r^{-1}-T_i^{-1}}{\ln[(1-x_r)/(1-x_i)]}$	$\frac{\ln[(dx/dt)_r/(dx/dt)_i]}{\ln[(1-x_r)/(1-x_i)]}$	720	1.1
Coats and Redfern [30]	T^{-1}	$\ln\left[\frac{-\ln(1-x)}{T^2}\right]$	850	1
Kissinger [24]	T_m^{-1}	$\ln\left(\frac{dT/dt}{T_m^2}\right)$	600	1

[a] This method uses both the analyzed set of data (i) as well as a reference set of data (r).
T: temperature in K.
x: fraction transformed.
t: time.
T_m: temperature of peak maximum in K.

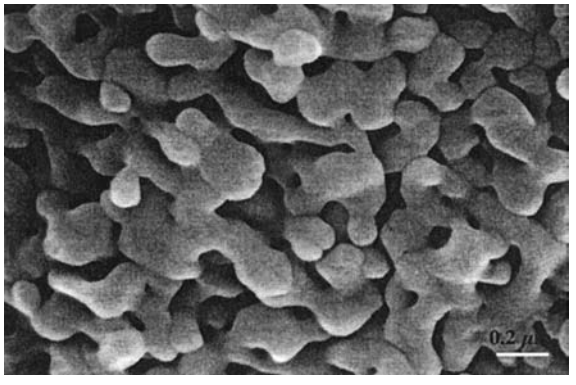

Fig. 3. Vermicular microstructure of boehmite-derived α-Al_2O_3 (1300°C, 100 min).

phase transformation is first order. This conclusion is supported by the dendritic or vermicular growth process that occurs during the transformation, shown in Fig. 3.

The Kissinger equation is

$$\ln\left[\frac{(dT/dt)}{T_m^2}\right] = \frac{-E_a}{R}\left(\frac{1}{T_m}\right) + B \quad (1a)$$

$$B = \ln\left(\frac{AR}{E_a}\right) = \text{constant} \quad (1b)$$

where T is the temperature in K, t is time, T_m is the peak maximum temperature of the phase transformation, E_a is the activation energy, A is the Arrhenius constant, and R is the gas constant. By plotting $\ln[(dT/dt)/T_m^2]$ vs. $(1/T_m)$ for various heating rates, one can obtain the activation energy from the slope, $-E_a/R$.

It has been shown previously that the seed number density, not the seed weight addition, is the more useful variable for understanding how seeding affects the transformation kinetics and microstructural evolution during the θ to α-Al_2O_3 phase transformation [5]. Fig. 4 shows the seed number density, f_s, as a function of seed size, d_s, for various seed concentrations according to the following equation:

$$f_s = \frac{N_s}{V_{tot}} = \frac{6m_\alpha}{\pi\rho_\alpha V_{tot}} \sum_{i=1}^{n} \frac{wf_i}{d_i^3} \quad (2)$$

where N_s is the number of seeds, V_{tot} is the total volume of the powder, m_α is the weight of the seeds added, ρ_α is the theoretical density of the seeds, and d_i is the seed size for a given weight fraction, wf_i. According to Kumagai and Messing, the optimum seed number density for controlling the microstructural evolution and transformation kinetics during the θ to α-Al_2O_3 phase transformation is 5×10^{13} seeds/cm^3 γ-Al_2O_3 [5]. Further increases in the seed number density did not result in any appreciable reduction in the θ to α-Al_2O_3 transformation temperature. The dark shaded area indicates the regime, where the seed

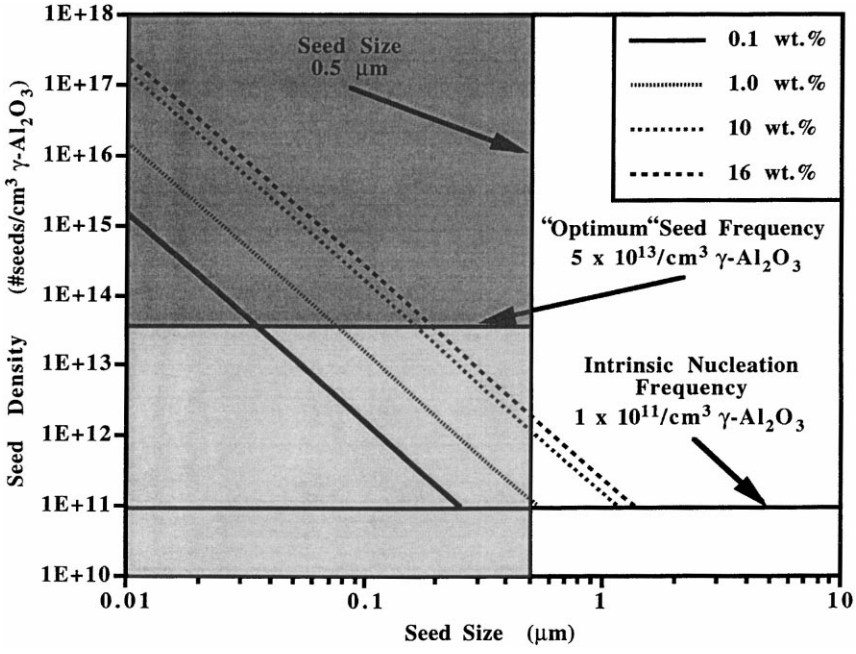

Fig. 4. Seed density as a function of seed size at various seed concentrations.

size is <0.5 μm and the seed number density is $>5\times10^{13}$ seeds/cm^3 γ-Al_2O_3. From Fig. 4 it is shown that, at 16 wt.% seeds (percolation limit), the seed particles must be ≤0.2 μm in order to be effective during the phase transformation. To obtain the same number density with 0.1 wt.% seed particles, the seed size would have to be ≤30 nm. Also plotted in the figure is the intrinsic nucleation density for alumina, 1×10^{11} nuclei/cm^3 γ-Al_2O_3, the highest value reported in literature [13]. It can be seen from the figure that at a seed concentration of 1 wt.%, seed particles ≥0.5 μm do not affect the nucleation density. Thus, the addition of a particular wt.% seed particles, which corresponds to a critical number density, is an important criterion for seeded alumina transformations. The above analysis assumes the seed particles are discrete particles and are not agglomerated. By using boehmite sols, investigators ensure that the boehmite was dispersed, too. As shown below, homogeneity of the seed distribution is key to obtaining beneficial effects from seeding.

From the previous investigation, it is obvious that the number concentration of α-Al_2O_3 seeds, the homogeneity of the seed distribution in the boehmite or transition alumina matrix, and the purity of the starting materials have significant effects on the transformation kinetics. The objective of this study is to investigate these variables using commercial powders. The use of commercial powders, which are inherently agglomerated, limits the attainable homogeneity of the seed distribution, but it avoids the costly and time intensive preparation of high purity sols from alkoxide precursors.

2. Experimental Procedure

The boehmite sols were prepared from a commercial alkoxide-derived alumina sol[1]. Ten weight percent boehmite hydrosols were produced by adding deionized water. The characteristic pH of the sol was 4.4 due to the nitric acid added by the manufacturer. To stabilize the dispersion and reduce the boehmite agglomerate size, the sol was stirred and periodically sonicated for 3 days. The dispersed 'particle' size,

[1]Disperal Sol P2, CONDEA Chemie GmbH, Hamburg, Germany.

determined by dynamic light scattering[2], was ≈50 nm. This indicates that the boehmite crystallites of 5 nm cluster to this size.

A nanocrystalline fumed γ-Al_2O_3 powder[3], produced by frame hydrolysis of aluminum chloride, was also used. A 2.5 wt.% dispersion was prepared by adding the γ-Al_2O_3 to deionized water and adjusting the pH to 3.0 with 2M nitric acid. The dispersed agglomerate size, determined by dynamic light scattering[2] was ≈86 nm.

Commercial α-Al_2O_3 powder was used to obtain fine particulate seeds[4]. An α-Al_2O_3 dispersion was prepared by adding ten weight percent α-Al_2O_3 powder to deionized water and adjusting the pH to 3.0 with 2M nitric acid. The dispersion was stirred for 3 days and periodically sonicated to break up agglomerates. The seeds were obtained by removing the supernatant of the dispersions after centrifugation at a force equivalent to 23 times the force of gravity (45 min, 2000 rpm, 0.2 m radius). The seed dispersion was added to the boehmite sol and the γ-Al_2O_3 dispersion while stirring to obtain seed concentrations of 0, 0.1, 1.25, 2.5, and 5 wt.% α-Al_2O_3, on a γ-Al_2O_3 weight basis. The seeded sols were dried and gelled by rapid dehydration in a rotary evaporator to prevent gravimetric segregation of the α-Al_2O_3 seeds during drying.

After drying, the seeded powders were ground into agglomerates <45 μm (#325 mesh) with a high purity alumina mortar and pestle. For investigation on the effect of seed concentration on the phase transformation kinetics, sieved powder was uniaxially pressed at 280 MPa in a hardened steel die that was lubricated with zinc stearate. The pellets were then cold isostatically pressed[5] in latex bags at 280 MPa for 30 min. The pellet dimension were 6.2 mm diameter and ≈3 mm height. The green densities of the pressed pellets, determined by the dimensional technique, were 60% and 54%, based on the boehmite and γ-Al_2O_3 theoretical densities of 3.01 g/cm^3 and 3.2 g/cm^3, respectively [1]. To transform the boehmite to γ-Al_2O_3, the pellets were calcined in air at 2°C/min to 550°C for 5 h. To investigate the effect of green density on the transformation kinetics, sieved, 5 wt.% α-Al_2O_3 seeded γ-Al_2O_3 powder was unaxially pressed at 140, 280, 420, and 560 MPa in zinc stearate lubricated WC die. The pellet dimensions were 6.2 mm diameter and ≈2 mm height. The green densities of the pressed pellets, determined by the dimensional technique, were 48, 53, 56, and 59% theoretical density (3.2 g/cm^3) for samples pressed at 140, 280, 420, and 560 MPa, respectively.

The effect of seed concentration and green density on the θ to α-Al_2O_3 phase transformation temperature was investigated using differential thermal analysis (DTA)[6]. DTA samples were obtained by breaking pressed pellets into ≈25 mg pieces. The fragments were heated in Pt cups at 10°C/min to 850°C, and then at the desired heating rate to 1300°C.

In order to determine the reproducibility of the data, one experimental condition from each set of experiments was repeated. In all cases, the variability of the data was <1%.

3. Results and Discussion

The particle size distribution of the seed particles as determined by centrifugal sedimentation[7] is shown in Table 2. There is some agglomeration of the seeds in the 100–200 nm size range, however, a significant portion of the number of the seeds is <60 nm. For the sake of calculation, the particles <50 nm are assumed to have an average particle size of 25 nm. The size distribution was validated by inspection of the seeds using transmission electron microscopy (TEM)[8], shown in Fig. 5. Due to the preparation technique of the sample (evaporation of seed sol on TEM grid), the particles have agglomerated on the slide. However, the particles are still distinguishable and appear to be discrete single crystals ranging from 20 to 60 nm in size. Crystallite sizes were determined by X-ray line broadening using the Scherrer equation:

$$d = \frac{0.9\lambda}{B\cos\theta}, \quad B = (B_0^2 - B_c^2)^{1/2} \tag{3}$$

where B_0 is the full-width at half-maximum (FWHM)

[2]Microtrac UPA, Leeds and Northrup, St. Petersburg, FL.
[3]Aerosil® Aluminum Oxide C, Degussa, Ridgefield Park, NJ.
[4]Taimei DAR, Taimei Chemical Industrial, Nagano, Japan.
[5]Cold Isostatic Press, Autoclave Engineers, Erie, PA.
[6]Model 1600 DTA. TA Instruments, Newcastle, DE.
[7]Model CAPA-700, Horiba Instruments, Irvine, CA.
[8]Model EM 420T, Phillips, Netherlands.

Table 2
Particle size distribution of α-Al_2O_3 seeds obtained from taimei DAR powder

Particle diameter (nm)	Volume frequency (%)	Number frequency (%)
300–400	0.1	0.0001
200–300	4.2	0.01
100–200	29.4	0.34
90–100	0.6	0.03
80–90	3.1	0.19
70–80	3.2	0.29
60–70	5.3	0.74
50–60	15.6	3.61
<50	38.5	94.8

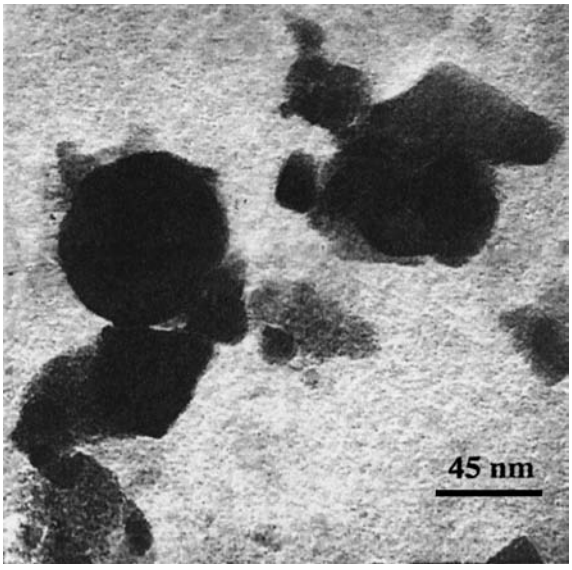

Fig. 5. TEM micrograph of Taimei DAR α-Al_2O_3 seeds.

(in $^\circ 2\theta$), B_c is the correction factor for instrument broadening, θ is the peak maximum (in $^\circ 2\theta$), and λ is the Cu K_α weighted average wavelength. Based on this analysis, the crystallite sizes of the boehmite, γ-Al_2O_3, and the α-Al_2O_3 seed particles were 5, 6.5, and 37 nm, respectively. For the α-Al_2O_3 seeds, the TEM and X-ray analysis techniques show consistent results with the particle size distribution given in Table 2. Therefore, the seed number density can be calculated with a high degree of confidence from the seed concentration and particle size distribution, using Eq. (2). The seed number densities for γ-Al_2O_3 (and boehmite after calcination to γ-Al_2O_3) calculated from the sedimentation data are shown in Table 3. At a seed concentration of 0.1 wt.%, the seed number density is 4×10^{13} seeds/cm^3 γ-Al_2O_3 and the number density increases to 2×10^{15} seeds/cm^3 γ-Al_2O_3 at a seed concentration of 5 wt.%.

Table 3
Calculated seed number density for various seed concentrations

Seed concentration (wt.%)	# Seeds/cm^3 γ-Al_2O_3
0.1	4×10^{13}
1.25	5×10^{14}
2.5	1×10^{15}
5	2×10^{15}

The analytical data, including phase identity, specific surface area, and impurities (from inductiveley coupled plasma spectral analysis) of the as-received powders are shown in Table 4. From the previous investigation, it was shown that Fe and Ti can promote nucleation of the θ to α-Al_2O_3 phase transformation. However, in this investigation, the impurity levels are significantly less than the levels previously investigated. If the impurities are considered to be present in the material as 50 nm oxide seeds, the corresponding seed number density would be $<5\times10^{11}$ seeds/cm^3

Table 4
Analytical data of the as-received powders

	Condea disperal sol P2	Aerosil® Alon C	Taimei DAR
Crystal phase	Boehmite	γ, δ-Al_2O_3	α-Al_2O_3
Specific surface area (m^2/g)	281	115	14
Al_2O_3 content (%)	70.8	96 (4% H_2O)	99.99
Nitrate content (%)	4.8	—	ND
HCl content (%)	ND	<0.5	ND
Ca (ppm)	ND	ND	1[a]
Cr (ppm)	ND	ND	<1[a]
Fe (ppm)	117[a]	320[b]	8[a]
K (ppm)	ND	ND	2[a]
Mg (ppm)	ND	ND	1[a]
Mn (ppm)	ND	ND	<1[a]
Na (ppm)	2[a]	ND	5[a]
Si (ppm)	42[a]	<170[b]	15[a]
Ti (ppm)	6[a]	390[b]	ND

ND: denotes not detected within the limits of the analysis technique.
[a] Supplied by manufacturer.
[b] Measured.

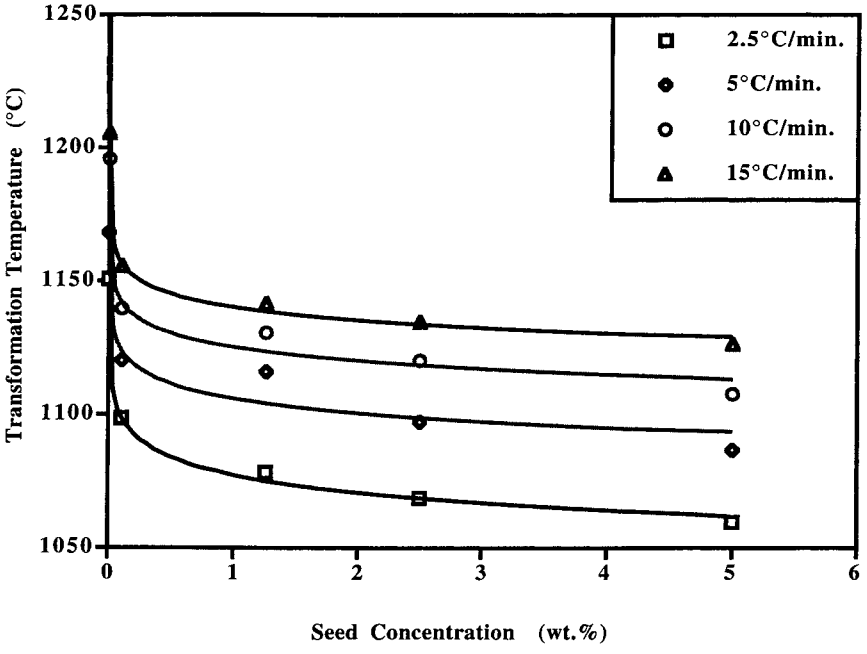

Fig. 6. θ to α-Al_2O_3 phase transformation temperature for seeded boehmite gels at various heating rates.

γ-Al_2O_3. Since the seed number densities used for this investigation are orders of magnitude greater, the effects of the Fe and Ti impurities are assumed to be negligible. Si impurities have been shown to inhibit the θ to α-Al_2O_3 phase transformation; however, the temperature investigated and level of impurities in this investigation are relatively low (<200 ppm).

The peak temperature for θ to α-Al_2O_3 phase transformation in boehmite samples, at various heating rates, are plotted as a function of seed concentration in Fig. 6. At the slowest heating rate of 2.5°C/min, the unseeded sample transforms at 1150°C and decreases to 1060°C with 5 wt.% α-Al_2O_3. At the highest heating rate of 15°C/min the unseeded sample transforms at 1205°C and decreases to 1130°C at 5 wt.% α-Al_2O_3. At all heating rates, there is a significant decrease in peak temperature (≈50°C) for seed concentration of 0.1 wt.% α-Al_2O_3 (4×10^{13} seeds/cm^3 γ-Al_2O_3). The transformation temperature decreases an additional ≈35°C, when the seed concentration is increased to 5 wt.% (2×10^{15} seeds/cm^3 γ-Al_2O_3). Kumagai and Messing observed similar results for α-Al_2O_3 seeded boehmite system; however, they stated that the matrix was saturated at a concentration of 1.5 wt.% (5×10^{13} seeds/cm^3 γ-Al_2O_3), and that increasing the seed concentration may cause agglomeration of the seeds and thus decrease the benefits of additional seeds [5]. By carefully processing the powders to avoid agglomeration of the seeds, seed concentrations >1.5 wt.% may prove to have further benefits. Due to the smaller seeds used in this investigation, the seed frequency obtained at 1.25–5 wt.% seed additions is an order of magnitude greater than previous investigations.

The peak temperatures for the θ to α-Al_2O_3 phase transformation in γ-Al_2O_3 samples, at various heating rates, are plotted as a function of seed concentration in Fig. 7. At the slowest heating rate of 2.5°C/min the unseeded sample transforms at 1155°C and decreases to 1075°C and decreases to 1075°C with 5 wt.% α-Al_2O_3. At the highest rate of 15°C/min the unseeded sample transforms at 1210°C and decreases to 1140°C at 5 wt.% α-Al_2O_3. At all heating rates, the most significant decrease in peak temperature (≈60°C) occurs at a seed concentration of 1.25 wt.% α-Al_2O_3. The transformation temperature decreases an additional ≈15°C, when the seed concentration is increased to 5 wt.%. This behavior is similar to the seeded boehmite powders, with slightly higher (10°C) transformation temperature for the seeded γ-Al_2O_3

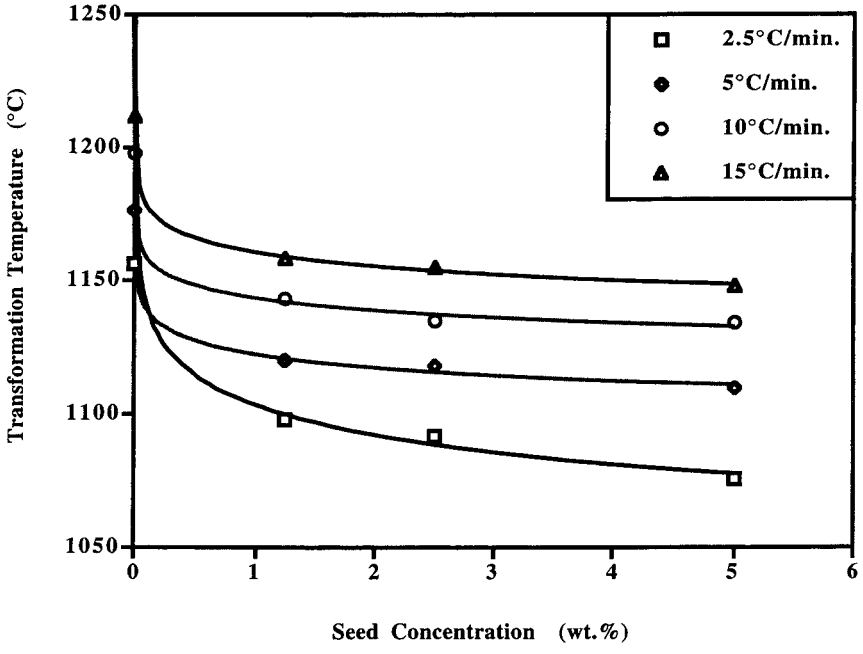

Fig. 7. θ to α-Al_2O_3 phase transformation temperature for seeded γ-Al_2O_3 powders at various heating rates.

powders. Tsai and Hsieh reported a phase transformation temperature of 1261°C for the same powder at a heating rate of 10°C/min, 65°C higher than the temperature observed in this investigation [12]. Their samples were prepared from colloidal gels of the fumed powder which had a bulk density of 1.1 g/cm^3 (37% of theoretical); however, the samples prepared for DTA experiments in this investigation had bulk densities of 1.17 g/cm^3 (58% of theoretical). The higher bulk density will result in an average higher particle coordination number of 4 vs. 7 for the more dense sample [32]. Increasing the number of matrix particles in contact with the seed particles reduces the transformation temperature. In the case of the seeded samples, a more homogeneous distribution of seeds in the matrix can be achieved in the boehmite system due to the smaller dispersed agglomerate size, 50 nm for the boehmite compared to 86 nm for the γ-Al_2O_3. This will increase the coordination number of matrix particles with seed particles, further lowering the transformation temperature.

In order to determine the effect of bulk density on the transformation temperature, DTA was conducted on 5 wt.% seeded γ-Al_2O_3 samples pressed at various pressures. The DTA peaks for the θ to α-Al_2O_3 phase transformation as a function of bulk density for 5 wt.% seeded γ-Al_2O_3 are shown in Fig. 8. As the bulk density increases, the position of the peaks moves to lower temperatures, the height of the peaks increases, and the width of the peaks decreases, indicating an increase in the rate of the phase transformation. The sample with the lowest bulk density of 47.6% transformed at 1157°C, and the sample with the highest bulk density of 59.1% transformed at 1132°C. An increase in bulk density of 11.5% lowered the transformation by 25°C. Therefore, in addition to controlling the homogeneity and number of seeds added, the sample density is also an important variable for controlling the transformation kinetics.

A plot of the θ to α-Al_2O_3 phase transformation data for boehmite samples, fit to Eq. (1a), is shown in Fig. 9. The activation energy calculated from the slope ($-E_a/R$) is given for the various seed concentrations. The unseeded boehmite has an activation energy of 522 kJ/mol. The activation energy was lowered to 487 kJ/mol at 0.1 wt.% seeds and to 420 kJ/mol at 1.25 wt.% seeds. Further increasing the seed concentration to 5 wt.% only lowered the activation to 406 kJ/mol. Due to the high degree of homogeneity possible in sol-gel processing, the matrix begins to saturate at a

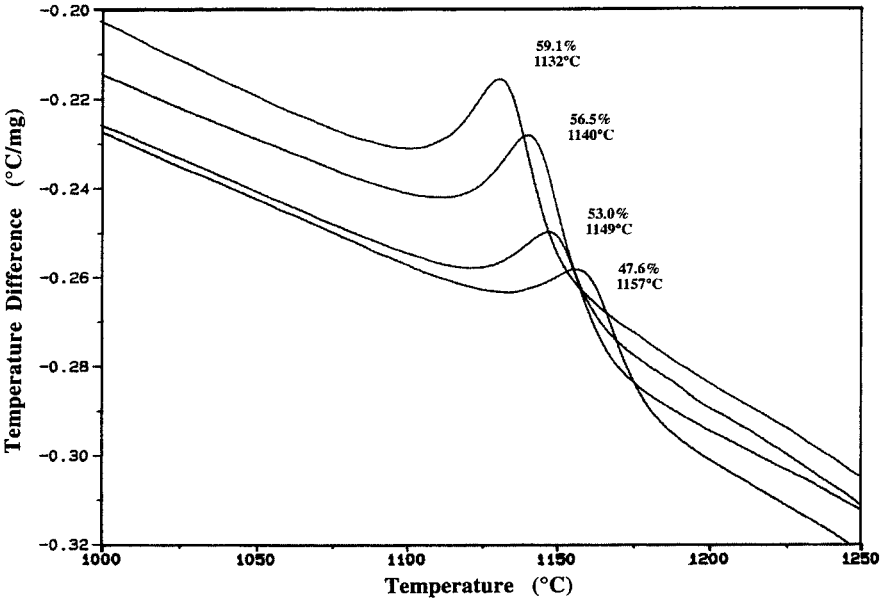

Fig. 8. DTA peaks of the θ to α-Al_2O_3 phase transformation in 5 wt.% seeded γ-Al_2O_3 as a function of green density.

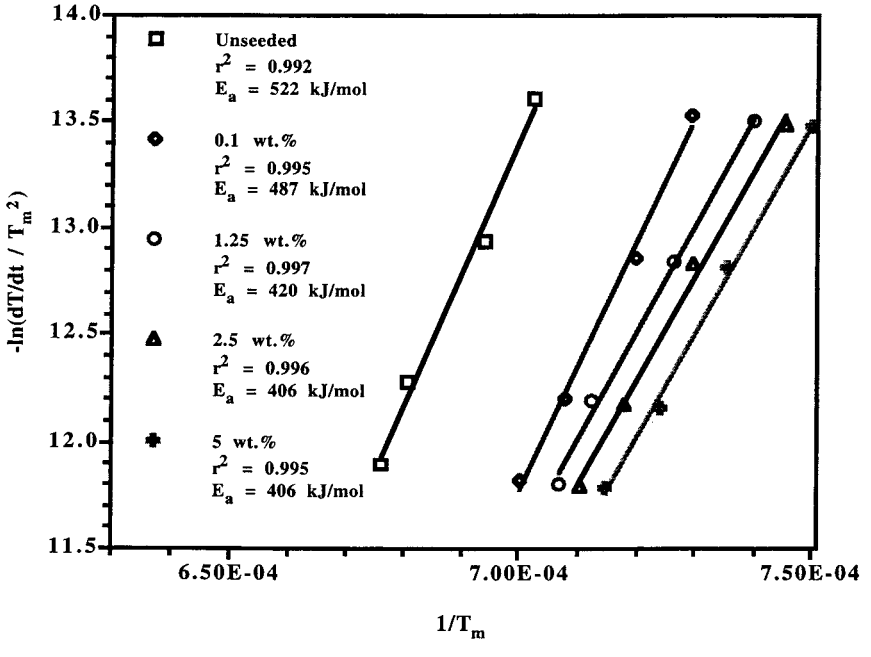

Fig. 9. Determination of the activation energy for θ to α-Al_2O_3 phase transformation in seeded boehmite powders.

seed concentration of 1.25 wt.% (5×10^{14} seeds/cm^3 γ-Al_2O_3) and thus, reduction of the activation energy is limited. The activation energy for the unseeded samples is consistent with Schaper and Van Reijen, and Yoldas who obtained 600 and 557 kJ/mol, respectively, using thermal analysis techniques [31,33].

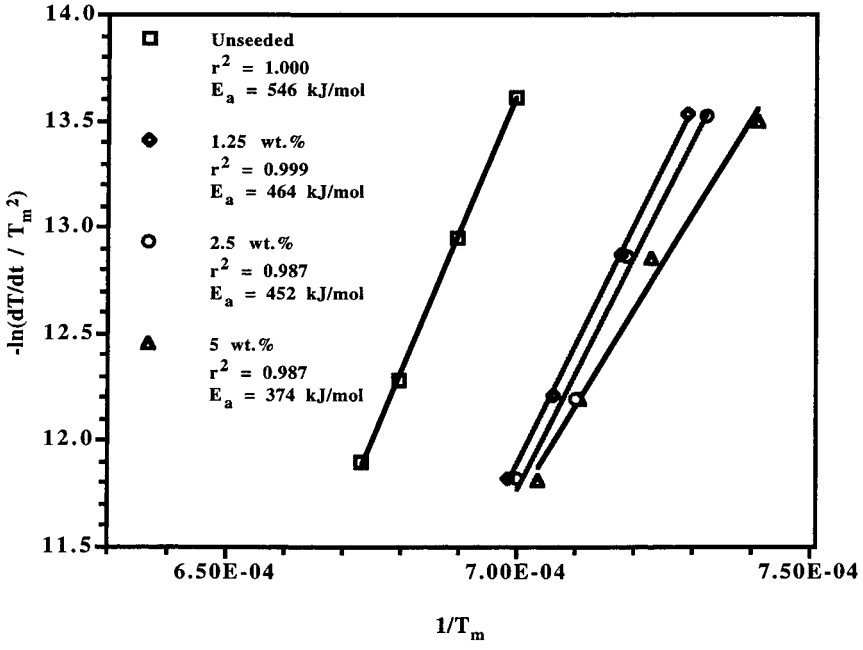

Fig. 10. Determination of the activation energy for θ to α-Al_2O_3 phase transformation in seeded γ-Al_2O_3 powders.

Another investigation of α-Al_2O_3 seeded boehmite using quantitative X-ray powder diffraction of isothermally treated powders reported activation energies of 431 kJ/mol and 360 kJ/mol for unseeded and 1.5 wt.% seeded powders, respectively [6]. The difference in analysis techniques may explain the difference in activation energies, but sample density and homogeneity differences may also be responsible.

A plot of the θ to α-Al_2O_3 phase transformation data for γ-Al_2O_3 samples, according to Eq. (1a), is shown in Fig. 10. The activation energy calculated from the slope ($-E_a/R$) is given for the various seed concentrations. The unseeded γ-Al_2O_3 has an activation energy of 546 kJ/mol while, the seeded γ-Al_2O_3 powders have lower activation energies of 461, 452 and 374 kJ/mol for the 1.25, 2.5, and 5 wt.% seeded samples, respectively. The activation energy was lowered by ≈85 kJ/mol at 1.25 and 2.5 wt.% seeds and an additional 85 kJ/mol at a 5 wt.% seed concentration. As mentioned earlier, since the dispersed powders could not be completely deagglomerated, the seed distribution is slightly heterogeneous, and thus, uniformity of seed distribution is limited to the scale of the γ-Al_2O_3 agglomerates. Due to the higher degree of agglomeration in the γ-Al_2O_3 powders, increasing the seed concentration to >2.5 wt.% further reduced the activation energy, as opposed to the case of the boehmite powders where the activation energy had already reached a plateau. The activation energies calculated in this investigation are consistent with other investigations using γ-Al_2O_3, which reported values of 486–640 kJ/mol [21,26]. The variations probably arise due to impurity, homogeneity, density, and analysis techniques.

4. Summary

The addition of α-Al_2O_3 seeds to commercial boehmite and γ-Al_2O_3 powders has been demonstrated to have a significant effect on the transformation kinetics. A seed concentration of 0.1 wt.% (4×10^{13} seeds/cm^3 γ-Al_2O_3) lowered the θ to α-Al_2O_3 phase transformation by ≈50°C and by ≈85°C at 5 wt.% seed concentration (2×10^{15} seeds/cm^3 γ-Al_2O_3) for boehmite samples. In the case of γ-Al_2O_3, the transformation temperature was lowered by ≈75°C at seed concentration of 5 wt.%(2×10^{15} seeds/cm^3 γ-Al_2O_3).

When the bulk density of 5 wt.% seeded γ-Al_2O_3 samples was increased from 47.6 to 59.1%, the transformation temperature was reduced an additional 25°C. The activation energy for the θ to α-Al_2O_3 phase transformation in boehmite samples decreased from 522 to 420 kJ/mol when seeded at $\geq$2.5 wt.%. The activation energy for γ-Al_2O_3 samples decreased from 546 to 452 kJ/mol at a seed concentration of 2.5 wt.%, and further reduced to 374 kJ/mol at a seed concentration of 5 wt.%. The data shows that there is a saturation in the effect of seed concentration at >2.5 wt.% (5×10^{14} seeds/cm^3 γ-Al_2O_3) for the phase transformation temperature and activation energy in boehmite samples. However, due to the higher degree of agglomeration in the γ-Al_2O_3 powders, further reductions are obtained at higher seed concentrations of 5 wt.% (2×10^{15} seeds/cm^3 γ-Al_2O_3).

Messing and Kumagai obtained similar results investigating 1.5 wt.% (5×10^{13} seeds/cm^3 γ-Al_2O_3) seeded boehmite [16]. The use of alkoxide derived, high purity boehmite avoided formation of agglomerates in the boehmite sols allowing for a homogeneous distribution of the seeds throughout the boehmite matrix. Although, the seed frequency was an order of magnitude greater for this investigation, the agglomeration inherent in commercial powders diminishes the effectiveness of the seeds. In order to improve the effectiveness of seeding in commercial powders, the agglomerate size must be further reduced or the larger agglomerates removed by gravitational setting techniques improving the homogeneity of the seed dispersion. In addition, attainment of high bulk densities will further increase the effectiveness of seeding.

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