

Enhanced transformation of gibbsite to α -alumina through mechanical activation

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Isothermal transformation kinetics was studied in mechanically treated and untreated gibbsite powders heated in air. The mechanical treatment enhanced the nucleation of α - Al_2O_3 , but did not affect the growth rate as evidenced by this similar values in the activation energy for transformation to α - Al_2O_3 of untreated and milled gibbsite. The accelerated transformation kinetics are believed to be due to the change in phase evolution during heating, as induced by the mechanical treatment. During heating the untreated powders, the δ and θ phases as a transition phase were observed but in the mechanically treated sample, the α and χ phases appeared. It has been found that a higher energy is needed for the $\Theta \rightarrow \alpha$ - Al_2O_3 transformation than for κ , $\chi \rightarrow \alpha$ - Al_2O_3 .

Key words: Mechanical activation, phase transformation kinetics, gibbsite, aluminum oxide phase transformation, ball-milling.

Introduction

Alumina is one of the most thoroughly studied ceramic materials because of its wide variety of applications. The transition of aluminum hydroxide to α - Al_2O_3 involves the formation of several Al_2O_3 intermediates, the nature of which depends on the type of aluminum hydroxide used as a precursor [1].

In order to completely convert gibbsite to α - Al_2O_3 , it is necessary to heat above 1200°C. However, it has been reported that mechanical treatment by high energy ball milling can induce the transformation of γ - Al_2O_3 or $\text{Al}(\text{OH})_3$ to α - Al_2O_3 and accelerate the transformation rate [2, 3]

Recently [4], we showed that the pretreatment of commercial gibbsite by milling significantly enhances α - Al_2O_3 formation. Moreover, α - Al_2O_3 powders prepared by the millings pretreatment were very fine compared with those prepared from as-received powders. The finer particles would be more effective to enhance sinterability. Previous mechanical treatment provides a unique method for controlling microstructural development during the transformation.

The onset temperature of formation of the α - Al_2O_3 is strongly related to the heating rate. Especially, under static conditions, the phase could be obtained at a temperature much lower than indicated by the thermal analysis. Further research on the kinetics of the transformation at low calcination temperatures could lead to advances in the fabrication of alumina. In addition an understanding of the completing kinetics of the α - Al_2O_3 formation will make it possible to take advantage

of the low temperature sinterability of mechano-chemically activated powders.

The present work attempts to characterize the low temperature calcination behavior of gibbsite powders with/without previous mechanical treatment in terms of their transformation kinetics and their structure.

Experimental Procedure

The starting powders used was commercial gibbsite (99.8% purity) which was produced by Korea general chemical co. using the Bayer process.

A planetary mill (Fritsch pulverisette 7) was used with zirconia balls and vials. The balls to powder weight ratio was 3 : 1. Alumina materials were not used as the grinding media, as they may cause a seed-effect due to the fine α -alumina powders introduced from alumina balls and vials during milling.

The gibbsite to α - Al_2O_3 transformation was examined by heating samples in Pt cups at a rate of 20°C/min in air in a DTA. Thermal treatments for the isothermal kinetics were conducted by placing a small amount of powder directly into the preheated furnace. After the required isothermal treatment time had elapsed, the powders was removed from the furnace and air quenched so that the cooling rate was very high.

The extent of α - Al_2O_3 transformation was followed by quantitative X-ray powder diffraction using monoclinic Zirconia as an internal standard [5].

Results and Discussion

The changes in XRD patterns of the gibbsite with ball milling time are shown in Fig. 1. Gibbsite was gradually amorphized by milling. It has been shown that the milling enhances dehydration [4, 6].

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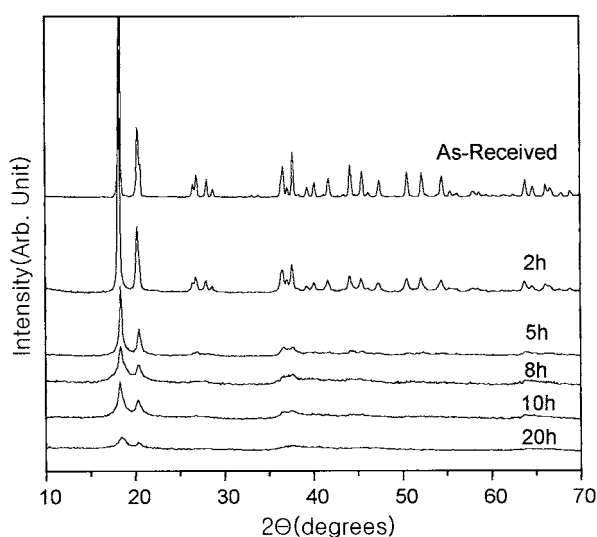


Fig. 1. X-ray diffraction patterns of aluminum hydroxide (gibbsite) with milling time. (milling times are noted)

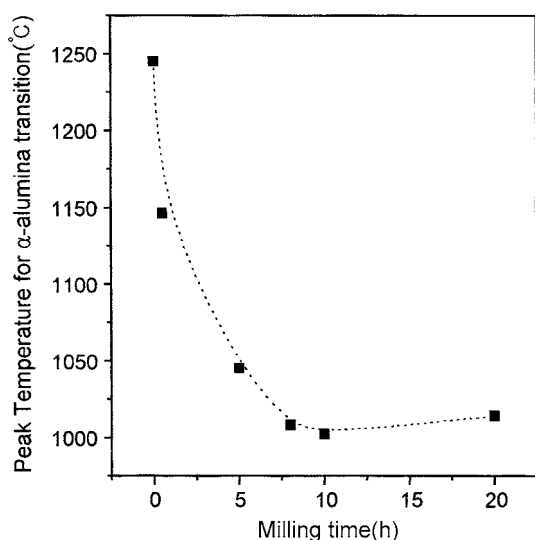


Fig. 2. Peak DTA temperature for aluminum hydroxides to α -alumina transformation as a function of milling time. (heating rate: $20^\circ\text{C}/\text{min}$)

Figure 2 shows the temperature of the $\alpha\text{-Al}_2\text{O}_3$ transformation as measured by DTA at $20^\circ\text{C}/\text{min}$ with milling time. The transformation temperature decreased from 1250°C before milling to about 1000°C after milling for 8h. The reduction in the transformation temperature seems to be saturated for further milling. It is clear that the previous mechanical treatment of gibbsite significantly enhances the gibbsite to $\alpha\text{-Al}_2\text{O}_3$ transformation, depending on the time of milling.

Although DTA provides a semiquantitative estimate of the effectiveness of mechanical activation on the $\alpha\text{-Al}_2\text{O}_3$ formation, a more quantitative understanding of the energetics of the transformation process can be obtained from a transformation kinetic analysis.

The isothermal transformation studies were conduct-

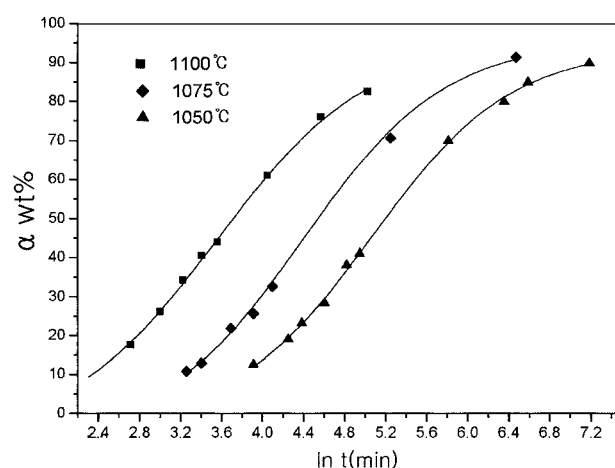


Fig. 3. Formation of α -alumina in as-received gibbsite powders annealed at different temperatures.

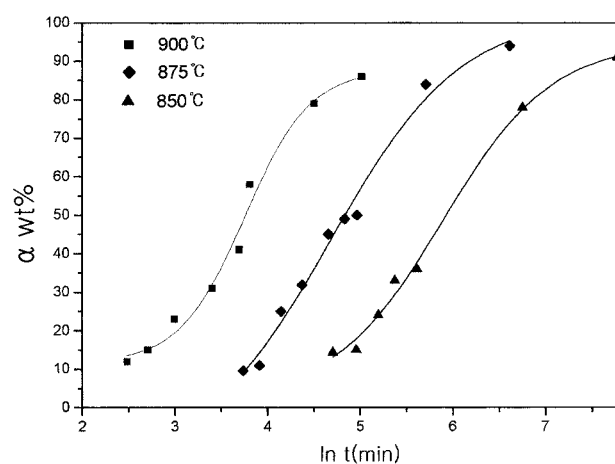


Fig. 4. Formation of α -alumina in as-received gibbsite powders ball milled for 8h and annealed at different temperatures.

ed in the range of temperatures below the $\alpha\text{-Al}_2\text{O}_3$ peak transformation temperature of the DTA. Figures 3 and 4 show the isothermal transformation data for gibbsite powders untreated and milled for 8h, respectively. It is clear that the isothermal rate curves appear to be sigmoidal, typical for Avrami-type transformation kinetics [7].

In order to quantify the transformation data, the Avrami model for nucleation and growth was applied. The volume fraction of the product phase ($\alpha\text{-Al}_2\text{O}_3$) after time t is given by

$$\alpha = 1 - \exp(-Kt)^n \quad (1)$$

where n is a constant dependent on the details of the nucleation and growth mechanisms, and K is the rate constant. For isothermal conditions, taking logarithms and rearranging Eq. (1) results in

$$\ln[-\ln(1-\alpha)] = n \ln K + n \ln t \quad (2)$$

where a plot of $\ln[-\ln(1-\alpha)]$ as a function of $\ln t$ yields the values of n and K . These plots are illustrated in

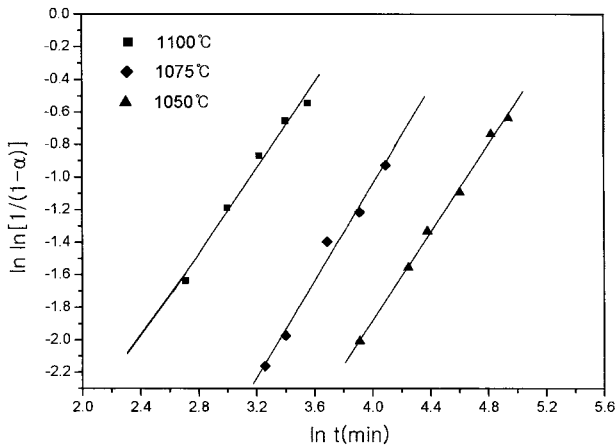


Fig. 5. Plot of $\ln \ln[1/(1-\alpha)]$ versus $\ln t$ for formation of α -alumina in as – received gibbsite powders.

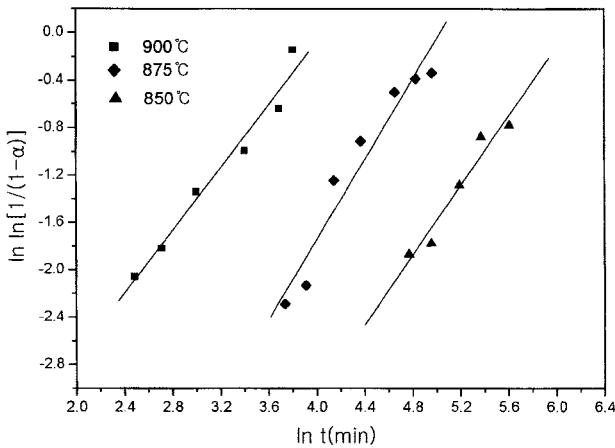


Fig. 6. Plot of $\ln \ln[1/(1-\alpha)]$ versus $\ln t$ for formation of α -alumina in as – received gibbsite powders ball-milled for 8h.

Figs. 5 and 6 for gibbsite untreated and milled for 8h, respectively. The kinetic data are presented in Table 1. The reaction rate constants for the overall transformation of gibbsite to α - Al_2O_3 follow an Arrhenius relationship over the temperature range examined, according to

$$K = A \exp(-E_a/RT) \quad (3)$$

where A is a constant, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. A

Table 1. Kinetic data obtained from Isothermal transformation analysis

Sample	Temp. (°C)	n	K
Untreated	1100	1.52	0.022595
	1075	1.48	0.009095
	1050	1.35	0.004748
Mechanically treated	900	1.32	0.017249
	875	1.69	0.0065388
	850	1.46	0.0023111

plot of $\ln K$ vs $1/T$ can be used to determine the activation energy for the transformation. The activation energies for the transformation to α - Al_2O_3 of untreated and milled gibbsites were 481 KJmol^{-1} and 442 KJmol^{-1} , respectively. The correlation coefficients were >0.99 for all of the activation energy plots. It has been reported in the literature that activation energies for the transformation to α - Al_2O_3 are in the range of $350\text{--}600 \text{ KJmol}^{-1}$ [8–10]. Direct comparisons of activation energies from different studies is problematic because of variations in experimental conditions and starting materials. The similar values in the activation energy may be because the data obtained for the range of transformed fraction from 10 to 60 wt% reflect mostly the α - Al_2O_3 growth process.

An overall macroscopic transformation which proceeds via a large number of atomic processes is exponentially related to the reciprocal of the absolute temperature and activation enthalpy and can be expressed by [11]

$$\text{rate} = v \exp(\Delta S/k) \exp(\Delta H/kT) \quad (4)$$

In condensed matter systems the activation enthalpy, ΔH , and the activation energy, E_a , are nearly the same. Therefore, the rate of the transformation may be expressed as an exponential function of an empirical activation energy, E_a , which is characteristic of the transformation process. The rate of transformation is also expected to depend upon the extent of transformation, α . Hence, the overall rate of the transformation process may be expressed by

$$d\alpha/dt = f(\alpha) K_0 \exp(-E_a/RT) \quad (5)$$

Integration of Eq. (4) and rearrangement of terms gives

$$\ln t_{\alpha 1} = \ln \left\{ \int [k_0 f(\alpha)]^{-1} d\alpha \right\} + E_a/RT \quad (6)$$

where $t_{\alpha 1}$ is the time required to obtain the fraction of the transformed product, α_1 .

The slope of the plot of the logarithm of time for a constant fraction of transformation against reciprocal of absolute temperature can be used for obtaining the value of E_a . Plots are given in Figs. 7 and 8 for untreated and milled gibbsites, respectively. Over selected intervals the derived plots are reasonably straight and parallel to each other, indicating that the α - Al_2O_3 formation in each case is characterized by a uniform mechanism, in the temperature interval investigated. The mean value of the activation energy determined from these plots is 455 KJmol^{-1} for untreated gibbsite and 444 KJmol^{-1} for the milled one. These values are comparable to those obtained by application of the Avrami equation.

We investigated the phase evolution during thermal treatment. Figure 9 shows the XRD patterns of untreated gibbsite powders calcined at 1075 as a function of time. After heat treatment for 26 min ($\sim 10\%$ transfor-

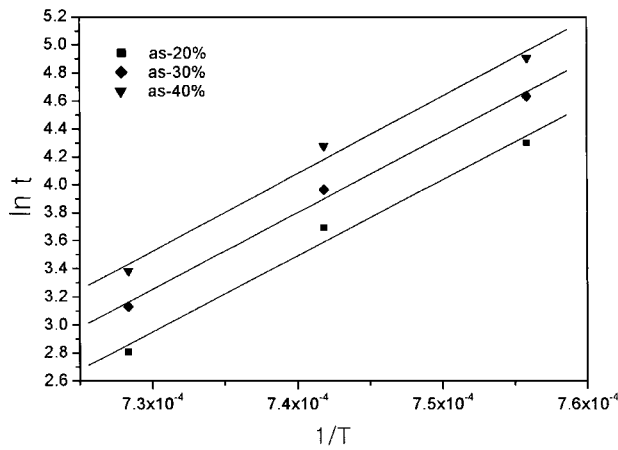


Fig. 7. The logarithm of time as a function of reciprocal temperature for various extent of α - Al_2O_3 formation in untreated gibbsite.

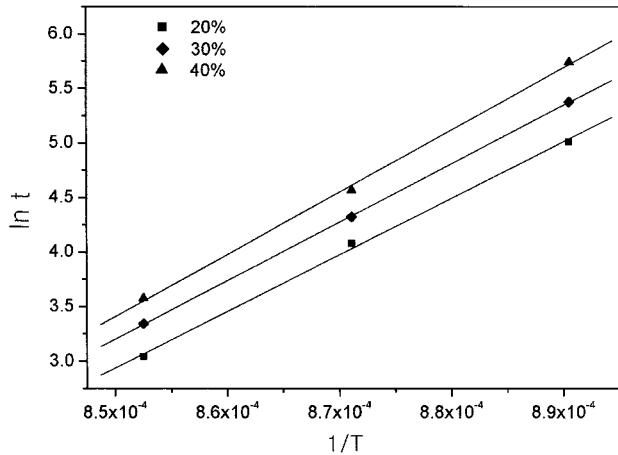


Fig. 8. The logarithm of time as a function of reciprocal temperature for various extent of α - Al_2O_3 formation in 8h ball-milled gibbsite.

mation), the α -phase was detected with δ and θ phases. The amount of α - Al_2O_3 increased with increasing heating time. However, it should be noted that the θ phase remained even after 644 min of heating ($\sim 91\%$ transformation). Similar behavior was observed for heating at 1100°C and 1050°C . On the other hand, in the case of mechanically treated powders traces of the κ and χ phases instead of the δ and θ phases were observed in the early stage of transformation. Figure 10 shows the XRD patterns of 8h ball-milled gibbsite heated at 875°C , as a function of heating time. These results show that a higher energy is needed for the $\theta \rightarrow \alpha$ - Al_2O_3 transformation than for κ , $\chi \rightarrow \alpha$ - Al_2O_3 . Therefore, it appears that the transformation kinetics accelerated by ball-milling is closely related to the change in the phase evolution during heating, as suggested in previous study [4]. At this point, it is worth noting that when the untreated gibbsite was heated at 850°C for 10h, the trace of α - Al_2O_3 in XRD pattern has

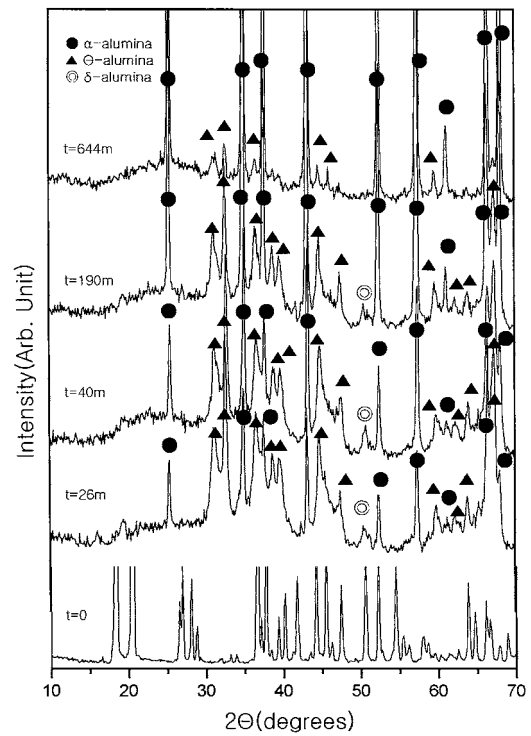


Fig. 9. X-ray diffraction patterns of the aluminum-hydroxide annealed at 1075°C for different times.

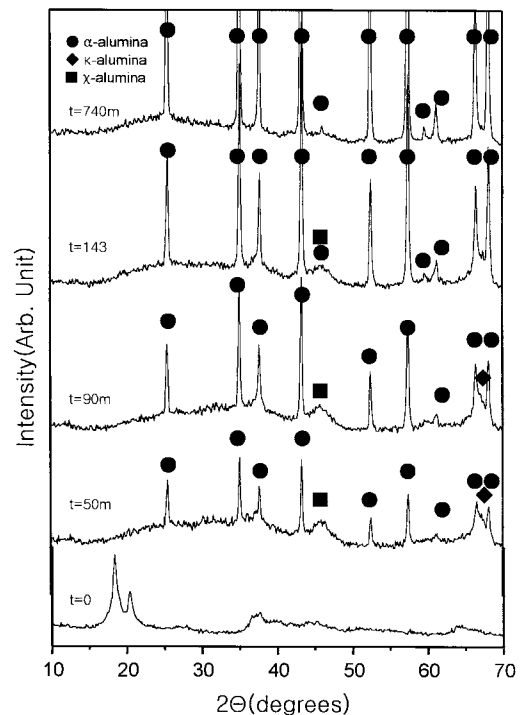


Fig. 10. X-ray diffraction patterns of the 8h-milled aluminum-hydroxide annealed at 875°C for different times.

not been observed, while 8h milled sample transformed by $\sim 15\%$ after heating for 100 min. This indicates that the mechanical treatment enhances the nucleation of α - Al_2O_3 .

Conclusions

The formation of α -Al₂O₃ in untreated and mechanically treated gibbsite occurs by a nucleation and growth process. The mechanical treatment is shown to enhance the nucleation of α -Al₂O₃, but do not affect the growth rate. The mechanical treatment changes the phase evolution during heating which lowers the gibbsite $\rightarrow$ α -Al₂O₃ transformation temperature and increases the transformation rate.

Acknowledgements

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