

# Phase Transformation of Mechanically Milled Nano-Sized $\gamma$ -Alumina

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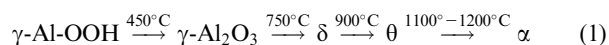
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**The phase transformation of mechanically milled nano-sized  $\gamma$ -alumina particles was investigated. The structures and phase presentation of the powders before and after milling were characterized using X-ray diffraction, transmission electron microscopy, and photoluminescence measurement. The phase transformation kinetics was investigated using differential scanning calorimetry. It was found that significant amounts of defects were generated by milling. These defects dramatically lowered the temperatures and activation energies of the transformation by promoting the nucleation and diffusion. The accumulation of the defects appears to show a logarithmic dependence of milling time.**

## I. Introduction

ALUMINA ( $\text{Al}_2\text{O}_3$ ) exists in eight different polymorphs—seven metastable phases ( $\gamma$ ,  $\delta$ ,  $\kappa$ ,  $\rho$ ,  $\eta$ ,  $\theta$ , and  $\chi$ ) and the thermally stable  $\alpha$ -phase. Metastable (also known as transition) alumina powders are intrinsically nanocrystalline in nature and can be easily synthesized by a variety of methods. For example,  $\gamma$ - $\text{Al}_2\text{O}_3$  can be obtained by thermal decomposition of boehmite ( $\gamma$ - $\text{Al}(\text{OOH})$ ) above  $450^\circ\text{C}$ .<sup>1</sup> Upon heating,  $\gamma$ - $\text{Al}_2\text{O}_3$  undergoes a series of polymorphic phase transformations from a highly disordered cubic close-packed lattice to the more ordered cubic close-packed  $\theta$ - $\text{Al}_2\text{O}_3$ . At higher temperatures, e.g.,  $1100^\circ$ – $1200^\circ\text{C}$ ,  $\theta$ - $\text{Al}_2\text{O}_3$  undergoes a reconstructive transformation to form the thermodynamically stable hexagonal close-packed  $\alpha$ -phase. Generally, this transformation sequence may be illustrated as follows:<sup>2,3</sup>



It is believed that the transformation of  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  is achieved by a nucleation and growth mechanism and belongs to the class of first-order phase transformation.<sup>4,5</sup>

Mechanical milling (also commonly known as high-energy ball milling) has been widely used to prepare a variety of non-equilibrium phases including nanocrystalline metallic and ceramic materials, amorphous alloys, and others.<sup>6–9</sup> Previous studies revealed that the phase transformation described in Eq. (1) can be triggered by mechanical milling. Kostić *et al.*<sup>10</sup> studied the phase transformation of  $\gamma$ -alumina during ball milling in a Fritsch Pulverisette mill and showed that the phase transforma-

tion sequence was  $\gamma \rightarrow \delta \rightarrow \theta$ . The authors attributed this transformation to the temperature rise during ball milling, which was estimated to be about  $1000^\circ\text{C}$ . The stable  $\alpha$ -phase did not form, however, because the required temperature of  $1200^\circ\text{C}$  was not reached. Zieliński *et al.*<sup>11</sup> also ball milled  $\gamma$ -alumina powders by cooling the milling vial with a fan. The temperature rise was controlled to 20 K. It was noted that after 2 h of milling, the  $\gamma$ -phase began to transform to the  $\alpha$ -phase. After 10 h of milling, the transformation was reported to be complete. A ball-milling-induced phase transformation in alumina has also been reported by others.<sup>12–17</sup> Some investigators attributed the phase transformations to the high pressures and high temperatures generated locally in the powder, while others attributed it to the high temperatures attained during the milling process. Recently, An and co-workers<sup>18</sup> studied the effect of  $\alpha$ -alumina seeds on the phase transformation of nano-sized  $\gamma$ - $\text{Al}_2\text{O}_3$  powders during ball milling. The ball milling was performed while cooling the milling vial with a fan. They found that the  $\gamma$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transformation only occurred in the specimens with seeds. Despite these contradictory results, a detailed study on the phase transformation of ball-milled alumina has not been performed.

In this study, we report on the phase transformation of ball-milled nano-sized  $\gamma$ -alumina powders. We find that ball milling can reduce the  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transformation temperature by up to 100 K for powders milled for 100 h. More interestingly, the activation energy of the phase transformation was reduced by more than 200 kJ/mol. Transmission electron microscopy (TEM), photoluminescence (PL), and X-ray diffraction (XRD) studies reveal that there is no observable decrease in powder size, but large amounts of defects were generated in the alumina powder during ball milling. The effect of such defects on the nucleation and growth during the phase transformation is discussed.

## II. Experiments

Commercially available  $\gamma$ -alumina powders of  $\sim 50$  nm from Dalian Luming Nanometer Material Ltd. (Dalian, China) were used in the present study. According to the provider, the purity of the powders, which was synthesized by thermal decomposition of boehmite ( $\gamma$ - $\text{Al}(\text{OOH})$ ), is 99.99%. The ball milling was carried out in a 2MZS-3 vibration mill (Xinkuang Grinding Machine Co, Wenzhou, China) at room temperature using stainless-steel balls of 12 mm diameter and a vial of 170 mm inner diameter. The ratio of the balls to powders was 15:1 by weight. The vials were cooled by a fan, and consequently, the temperature rise of the vial should be less than 50 K. Loading and unloading of the powders and milling were performed in high-purity Ar. The powders were ball milled at a frequency of 23 Hz for 2, 10, 50, and 100 h, respectively.

After milling, the powders were characterized using electron paramagnetic resonance (EPR) and Raman spectrometer. No signals corresponding to Fe have been observed, suggesting that the contamination level, if there is any, is negligible.

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The crystalline phases and the morphology of the powders before and after milling were characterized using XRD (Rigaku, Tokyo, Japan) with  $\text{CuK}\alpha$  radiation and TEM (Jeol JEM 2010F microscope). PL spectra of the as-received and ball-milled powders were recorded using a micro-zone Raman spectrometer with a UV lamp under the excitation of a 325 nm HeCd laser at room temperature.

The phase transformation of the as-received and ball-milled  $\gamma$ -alumina powders was studied using differential scanning calorimetry (DSC, SQT-600, TA instrument, New Castle, DE). The experiments were carried out in flowing  $\text{N}_2$  under various heating rates.

### III. Results

#### (1) Characterization of As-Received and Ball-Milled Powders

Figure 1 shows the XRD patterns of the  $\gamma$ -alumina powders in the as-received condition and after milling for different times. The characteristic peaks of  $\gamma$ -alumina at  $2\theta = 45.91^\circ$  for (400) and  $2\theta = 66.9^\circ$  for (440) remain even after milling for 100 h, suggesting that no phase transformation has occurred during ball milling. This result is consistent with our previous study,<sup>18</sup> but quite different from the other studies,<sup>10–17</sup> which showed that the phase transformation of  $\gamma$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  was complete in an even shorter milling time. Compared with the diffraction peaks from the as-received powder, the intensities of the peaks from ball-milled powders decrease, while the widths of the peaks increase slightly, which could be ascribed to the reduction in grain size or an increase in lattice strain and/or defects, or both.

TEM observation revealed that there is no significant change in the particle/grain size after ball milling, similar to the results of a previous study on similar powders.<sup>18</sup>

Further characterization of the  $\gamma$ -alumina powders was carried out by measuring their PL spectra (Fig. 2). The spectrum (Fig. 2(a)) of the as-received powders shows two peaks: a strong one centered at  $\sim 500$  nm and a weak one centered at  $\sim 780$  nm.

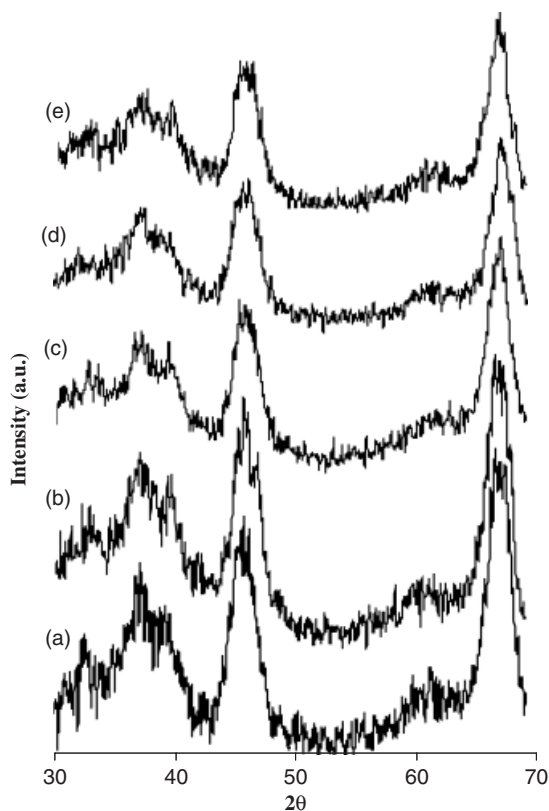


Fig. 1. X-ray diffraction patterns of the  $\gamma$ -alumina powders: (a) as-received and (b)–(e) ball milled for 2, 10, 50, and 100 h, respectively.

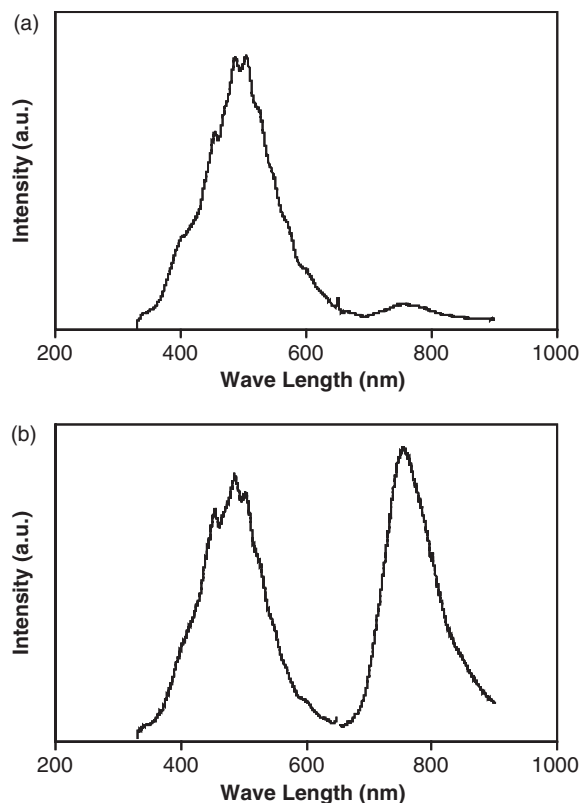


Fig. 2. Photoluminescence patterns of the  $\gamma$ -alumina powders: (a) as-received and (b) ball milled for 50 h.

The emission at 500 nm is ascribed to singly ionized oxygen vacancies (also known as  $\text{F}^+$  centers).<sup>19</sup> The strong emission (the green light can even be seen by the naked eye) suggests the existence of a large amount of the  $\text{F}^+$  centers in the as-received nano-sized  $\gamma$ - $\text{Al}_2\text{O}_3$  powders. The spectrum (Fig. 2(b)) of the  $\text{Al}_2\text{O}_3$  powders after ball milling for 50 h shows the same two peaks as the as-received powders. However, the intensity of the emission at 780 nm significantly increases to a level even higher than that for the emission at 500 nm. While the origin of the 780 nm emission is not clear at present, the remarkable increase in emission suggests that significantly large amounts of defects other than the  $\text{F}^+$  centers were generated during ball milling.

#### (2) Kinetics of Phase Transformation

The DSC profiles for  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transformation are plotted as a function of ball-milling time in Fig. 3. It can be seen

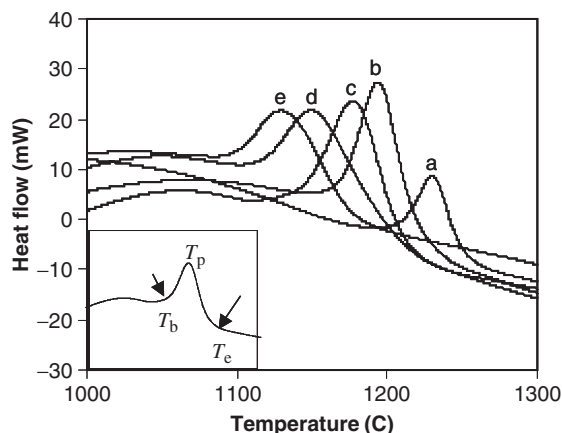


Fig. 3. Differential scanning calorimetry patterns of the powders: (a) as-received and (b)–(e) after ball milling for 2, 10, 50, and 100 h, respectively. Heating rate was  $15^\circ\text{C}/\text{min}$ .

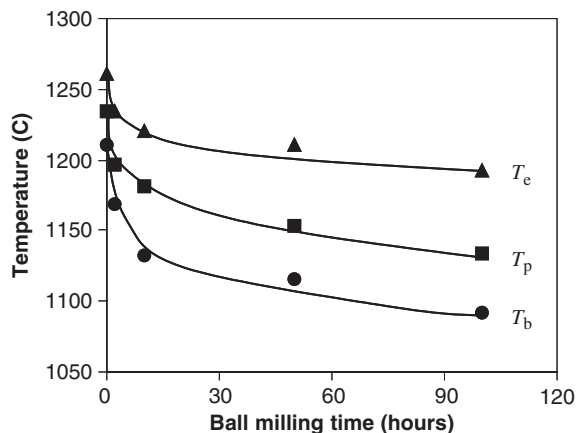


Fig. 4. Effect of ball milling time on the characteristic temperatures:  $T_b$ ,  $T_p$ , and  $T_c$ . The inset figure shows how to determine these temperatures.

that the exothermic peak shifts to lower temperatures as milling time increases, suggesting that the phase transformation becomes easier for ball-milled powders. For further understanding of the phase transformation, three characteristic temperatures are extracted from the profiles using the method shown in the inset figure: the temperature of the beginning of massive formation of  $\alpha$ - $\text{Al}_2\text{O}_3$  ( $T_b$ ); the peak temperature ( $T_p$ ); and the end-of-reaction temperature ( $T_c$ ). The variations in the characteristic temperatures as a function of ball-milling time are shown in Fig. 4. The results reveal that all three characteristic temperatures decrease with ball-milling time. The temperatures decrease rapidly for a shorter milling time and then taper off for long-term ball milling. At this heating rate ( $15^\circ\text{C}/\text{min}$ ), there is a significant decrease in both beginning temperature and peak temperature between the as-received powders and the powders after ball milling for 100 h: the differences are  $120^\circ$  and  $100^\circ\text{C}$ , respectively.

Figure 5 plots the duration of the  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transformation in terms of the temperature difference between  $T_c$  and  $T_b$  (or peak width,  $\Delta T = T_c - T_b$ ), which reflects the homogeneity of the phase transformation,<sup>20</sup> of the exothermic peaks as a function of ball-milling time. The duration increases with ball-milling time, suggesting less homogeneity of the transformation for ball-milled powders.<sup>20</sup> Again, the increase in the duration is more pronounced for short milling times.

The peak temperatures for different heating rates can be used to obtain the activation energy of the phase transformation according to the Kissinger equation by assuming that the peak maximum of the DSC curve represents the temperature of the

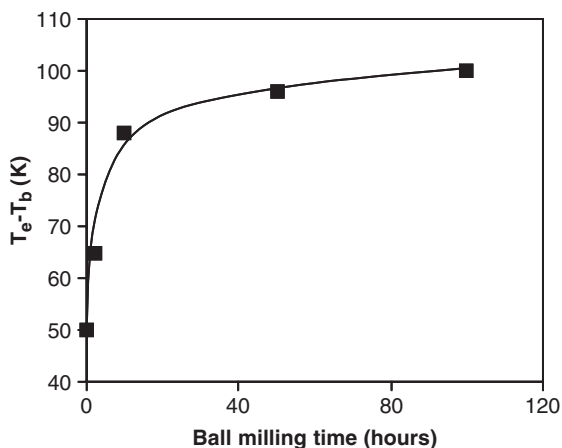


Fig. 5. Effect of ball-milling time on the temperature differences (peak width,  $\Delta T = T_c - T_b$ ).

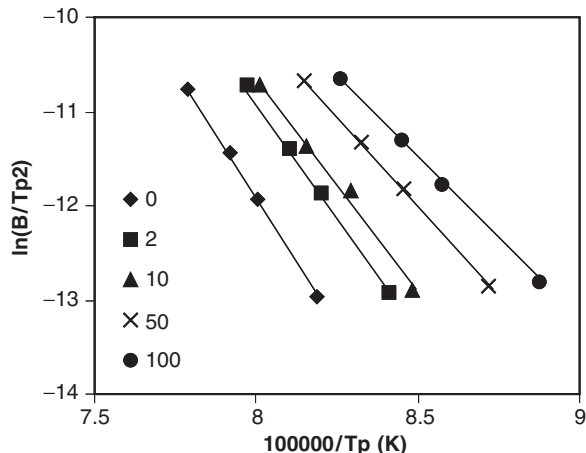


Fig. 6. Determination of the activation energy for  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transformation. The numbers indicate the ball-milling time.

maximum reaction rate:<sup>21</sup>

$$\ln\left(\frac{B}{T_p^2}\right) = -\frac{E}{RT_p} + C \quad (2)$$

where  $B$  is the heating rate,  $E$  is the activation energy, and  $C$  is a constant. Figure 6 shows the Kissinger plot for powders in the as-received condition and ball milled for 2, 10, 50, and 100 h, respectively. For each type of powders, the data were obtained at heating rates of  $5^\circ$ ,  $15^\circ$ ,  $25^\circ$ , and  $50^\circ\text{C}/\text{min}$ , respectively. These fairly good linear relationships were obtained for all powders and the activation energy can then be calculated from the slope ( $-E/R$ ). The results are plotted with respect to ball-milling time in Fig. 7. It can be seen that mechanical milling can dramatically reduce the activation energy. The as-received powder has an activation energy of  $563\text{ kJ/mol}$ , which is close to that reported previously.<sup>22</sup> The ball-milled powders have activation energies of 498, 450, 380, and  $354\text{ kJ/mol}$  for milling times of 2, 10, 50, and 100 h, respectively. The activation energy was significantly lowered by  $210\text{ kJ/mol}$  after 100 h milling. Figure 7 also reveals that the activation energy decreases rapidly for shorter milling time and then tapers off for longer milling time. As an example, the activation energy is reduced by  $65\text{ kJ/mol}$  after the first 2 h ball milling, but only reduced  $26\text{ kJ/mol}$  after the last 50 h of ball milling.

### (3) Sequence of Phase Transformation

To study the effect of ball milling on the sequence of phase transformations of the alumina powders, the as-received

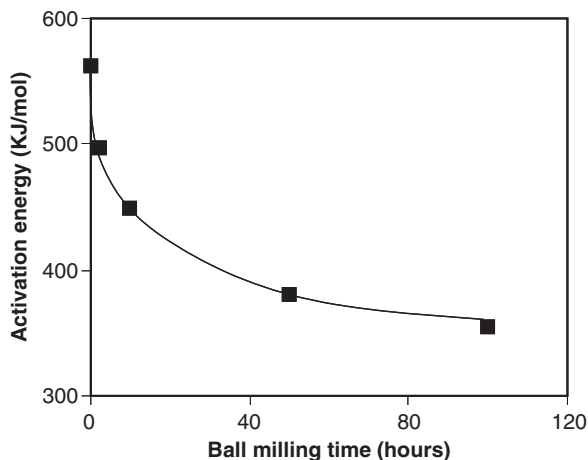
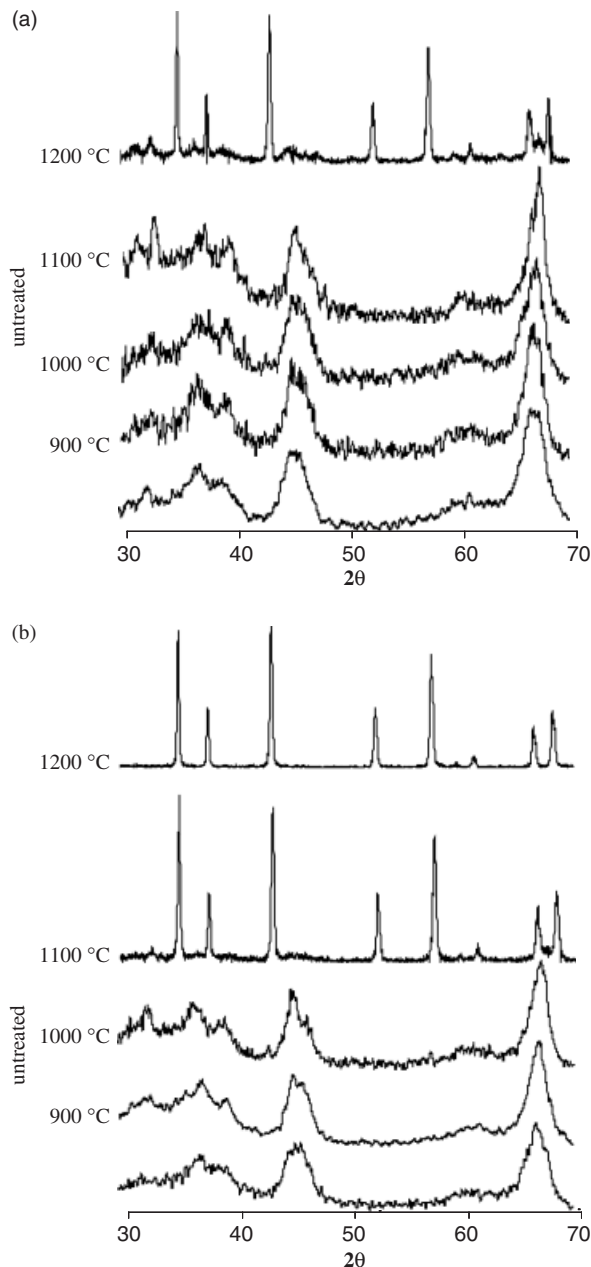


Fig. 7. Effect of ball-milling time on the activation energy of the  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transformation.

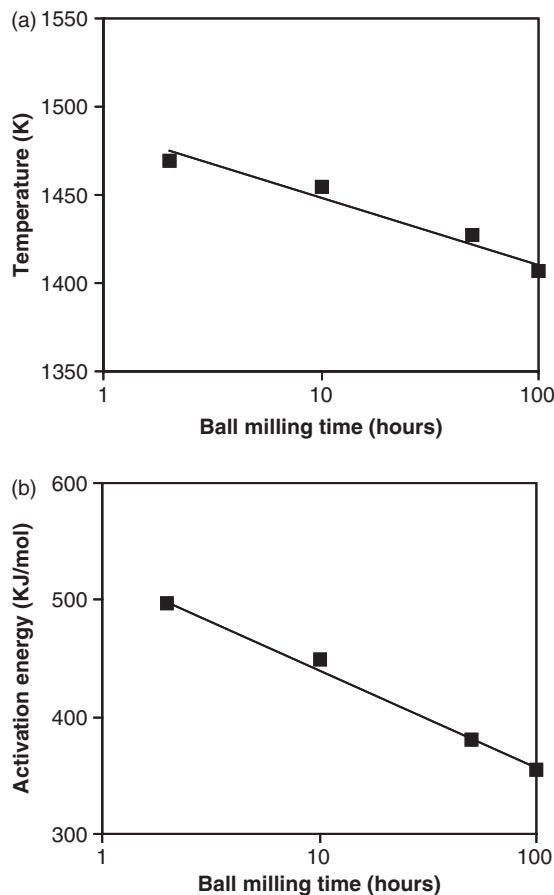


**Fig. 8.** X-ray diffraction patterns of (a) as-received powders and (b) powders after ball milling for 50 h after annealing at different temperatures for 1 h. The annealing temperatures are shown in the figures.

powders and the powders ball milled for 50 h were heat treated at different temperatures for 1 h. The phase representation was then characterized using XRD (Fig. 8). The phase content calculated from the XRD patterns is listed in Table I and clearly shows that regardless of ball milling, all powders follow the same transformation sequence:



However, the temperatures required for the transformation are different. Compared with unmilled powders, both  $\gamma$  to  $\theta$  and  $\theta$  to



**Fig. 9.** Peak temperatures (a) and activation energies (b) of the  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transformation as a function of ball-milling time.

$\alpha$  transformations occurred at much lower temperatures for ball-milled powders.

#### IV. Discussion

In this study, we demonstrate that the phase transformation of the  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  is dramatically affected by ball milling. Both temperatures and activation energies of the transformation decrease with ball milling time. The characterization of the powders before and after ball milling suggests that ball milling generates a large amount of defects. It is apparent that these defects promote the phase transformation. The  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  transformation is a first-order phase transformation. The overall rate of the transformation is controlled by the rates of nucleation and growth. Therefore, the activation energy of the transformation consists of two parts: one for nucleation and the other for diffusion. Separation of these two processes is difficult for the system studied here. The defects can affect both nucleation and growth processes by providing heterogeneous nucleation sites and fast diffusion paths, respectively. The sequence of the phase transformation is from  $\gamma$  to  $\theta$  and then to  $\alpha$ - $\text{Al}_2\text{O}_3$ ; the strong effect of ball milling of the  $\gamma$ - $\text{Al}_2\text{O}_3$  powders on the  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  transformation suggests that the defects generated in  $\gamma$ - $\text{Al}_2\text{O}_3$  powders were retained during the  $\gamma$ - to  $\theta$ - $\text{Al}_2\text{O}_3$  transformation.

The decreases in reaction temperatures and activation energies are non-linearly related to the ball-milling time. These

**Table I.** Phase Presentation in  $\gamma$ - $\text{Al}_2\text{O}_3$  Powders Heat-Treated at Different Temperatures

Annealing temperature ( $^{\circ}\text{C}$ )	900 $^{\circ}$	1000 $^{\circ}$	1100 $^{\circ}$	1200 $^{\circ}$
As-received	100% $\gamma$	100% $\gamma$	89.5% $\gamma$ +10.5% $\theta$	15.4% $\theta$ +84.6% $\alpha$
Ball milling for 50 h	100% $\gamma$	83.5% $\gamma$ +16.5% $\theta$	26.2% $\theta$ +73.8% $\alpha$	100% $\alpha$

results suggest that the formation of defects within the powders is not uniform during the milling. Figures 9(a) and (b) plot the peak temperatures and activation energies as a function of ball-milling time in logarithmic scale, respectively. Both curves show linear relationships, indicating the logarithmic dependence of the changes on milling time. Since both the peak temperature and activation energy should relate to the density of the defects generated during ball milling, we infer that the accumulation of the defects during ball milling may follow the same log dependence of ball-milling time.

### V. Summary

The high-energy ball milling of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> starting nanopowders has a significant effect on the transformation of  $\theta$ - to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Such an effect can be seen from the decrease in temperatures and activation energies of the transformation. The influence is attributed to the formation of defects, which were proved by the change in PL behavior of the powders before and after milling. We further demonstrated that the decreases in the temperatures and activation energies show a logarithmic dependence of the ball-milling time, suggesting that the defect density increases logarithmically with ball-milling time.

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