Phase transformation behaviors of aluminum hydroxides to alpha alumina in air and molten salt

JIA HE
School of Materials Science and Engineering, Shanghai University, Shanghai 200072, People's Republic of China

WEI LIU
Zhongzhou Branch China Aluminum Co., Ltd., Jiaozuo, Henan 454174, People's Republic of China

LI-HUI ZHU*
School of Materials Science and Engineering, Shanghai University, Shanghai 200072, People's Republic of China
E-mail: lhzhu@mail.shu.edu.cn

QING-WEI HUANG
The State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

Alpha alumina (α-Al_2O_3) is one of the most important materials in ceramic industry because of its unique chemical, electrical and mechanical properties [1]. α-Al_2O_3 powders for sintering are generally prepared by calcination of aluminum hydroxide ($Al(OH)_3$) due to relatively low cost of the raw material and manufacture process. However, high calcination temperature above 1200 °C is necessary for the transformation of $Al(OH)_3$ to α-Al_2O_3 in air. Molten salt synthesis (MSS) is a well-established method to form a desirable compound [2]. Owing to high diffusivities of the components in molten salt flux, the formation temperature and time can be reduced as compared with solid-state reaction [3]. The MSS method has never been reported to obtain α-Al_2O_3 in calcining aluminum hydroxide. This work intended to study the formation behaviors of α-Al_2O_3 from $Al(OH)_3$ in NaCl–KCl flux. In addition, it was reported that addition of ceramic oxide seed particles were effective to reduce the transformation temperature [4–7]. Thus, the influence of seeding on the transformation of $Al(OH)_3$ to α-Al_2O_3 in NaCl–KCl flux was also investigated.

A mixture of ultra-fine $Al(OH)_3$ (purity: 99.99%, surface area: 5 m^2/g, Zhongzhou Branch China Aluminum Co., Ltd.), NaCl and KCl (purity: 99.95%, Shanghai Chemical Company) in the weight ratio of 1:1:1 was used as starting material. The mixture was first ball-milled in ethanol for 3 hr with alumina balls, then dried and sieved through a 120-mesh screen. The dried powder was placed in a covered alumina crucible and calcined at 600–1200 °C for 4 hr. Afterwards, the powders were washed with de-ionized water until no chloride ions were detected. In order to study the effect of α-Al_2O_3 additives on the phase transformation of $Al(OH)_3$ to α-Al_2O_3 in molten salt, 5, 10 and 15 wt% high-purity Al_2O_3 (99.99%) particles were mixed in the starting mixture. Then the mixtures were balled, dried, calcined and washed according to the above-mentioned process. For comparison, aluminum hydroxide without any salt and seeds was calcined at 600–1500 °C for 4 hr. The phase transformation analysis of the calcined powders was based on X-ray diffraction data.

Fig. 1 shows the XRD patterns of aluminum hydroxide calcined at 600–1300 °C for 4 hr in air. The powders at 600 and 700 °C are composed of some amorphous phases. κ-Al_2O_3 phase begins at 800 °C. The powder calcined at 900 °C consists of main phase κ-Al_2O_3, a small amount of some amorphous phases and newly formed δ-Al_2O_3. When the temperature increases above 1000 °C, θ-Al_2O_3 phase forms accompanied by the disappearance of δ-Al_2O_3 and κ-Al_2O_3 phases is still the dominant phase. As the calcinations temperature further increases, α-Al_2O_3 phase begins at 1200 °C and is completely obtained above 1300 °C. It has been known that there are two different routes for the phase transformation of $Al(OH)_3$ to α- Al_2O_3 [8], which can be described as follows:

$$Al(OH)_3 \rightarrow \chi\text{-phase} \rightarrow \text{amorphous } Al_2O_3 \rightarrow \kappa\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \quad (1)$$

$$Al(OH)_3 \rightarrow AlOOH \rightarrow \gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \quad (2)$$

In this work, the phase transformation mainly takes place following the former path since κ-Al_2O_3 is the main phase before α-Al_2O_3 forms.

The XRD patterns of aluminum hydroxide with NaCl–KCl addition calcined between 600 and 1100 °C are shown in Fig. 2. The powders calcined at 600–900 °C are also composed of some amorphous phases and κ-Al_2O_3 phase. However, α-Al_2O_3 phase begins at 1000 °C and single-phase α-Al_2O_3 is obtained at 1100 °C, which is lower than in air. In comparison with the transformation behaviors without salt, δ- and

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*Author to whom all correspondence should be addressed.

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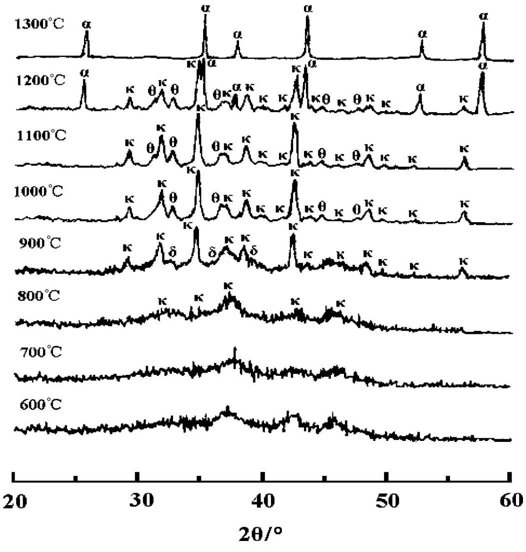

Figure 1 XRD patterns of aluminum hydroxide calcined at 600–1300 °C for 4 hr in air.

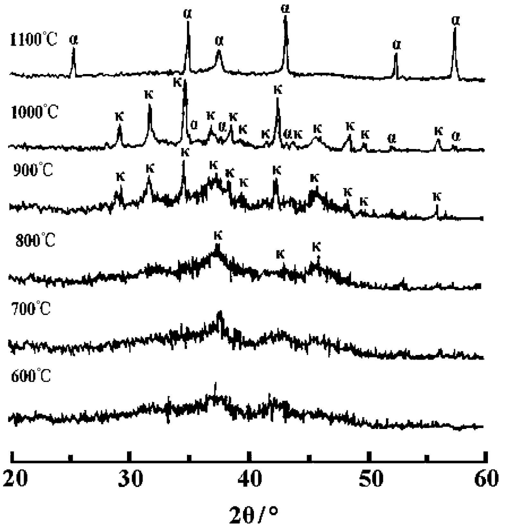

Figure 2 XRD patterns of aluminum hydroxide calcined at 600–1100 °C for 4 hr in molten salt.

θ-Al_2O_3 phases do not occur and therefore the phase transformation route is only according to route (1). Lower α-Al_2O_3 transformation temperature could be attributed to the decrease of the activation energy for phase transformation from κ-Al_2O_3 phase to α-Al_2O_3 phase and the increase of diffusivities of the components in the molten salt flux.

Fig. 3 shows the XRD patterns of calcined aluminum hydroxide in molten salt with various amounts of seed at 600–1000 °C. It can be seen that the addition of various seed content does not change the phase transformation route of $Al(OH)_3$ to α-Al_2O_3. However, the α-Al_2O_3 phase formation temperature decreases on increasing α-Al_2O_3 seed content and for the samples with 5, 10 and 15 wt% seeds it is 1000, 900 and 800 °C, respectively. These results indicate that seeding is also beneficial for the phase transformation. The α-Al_2O_3 phase transformation is according to nucleation and growth mechanism [9]. The addition of seeds, which are isostructural with α-Al_2O_3, provides low energy sites for nucleation and thus reduces the energy barrier required for nucleation [10]. As a result, the phase transformation can be complete at lower temperature. More seeds present more sites for nucleation, thus the transformation temperature can be lower. The results are similar to the previous work of Xie *et al.* [11].

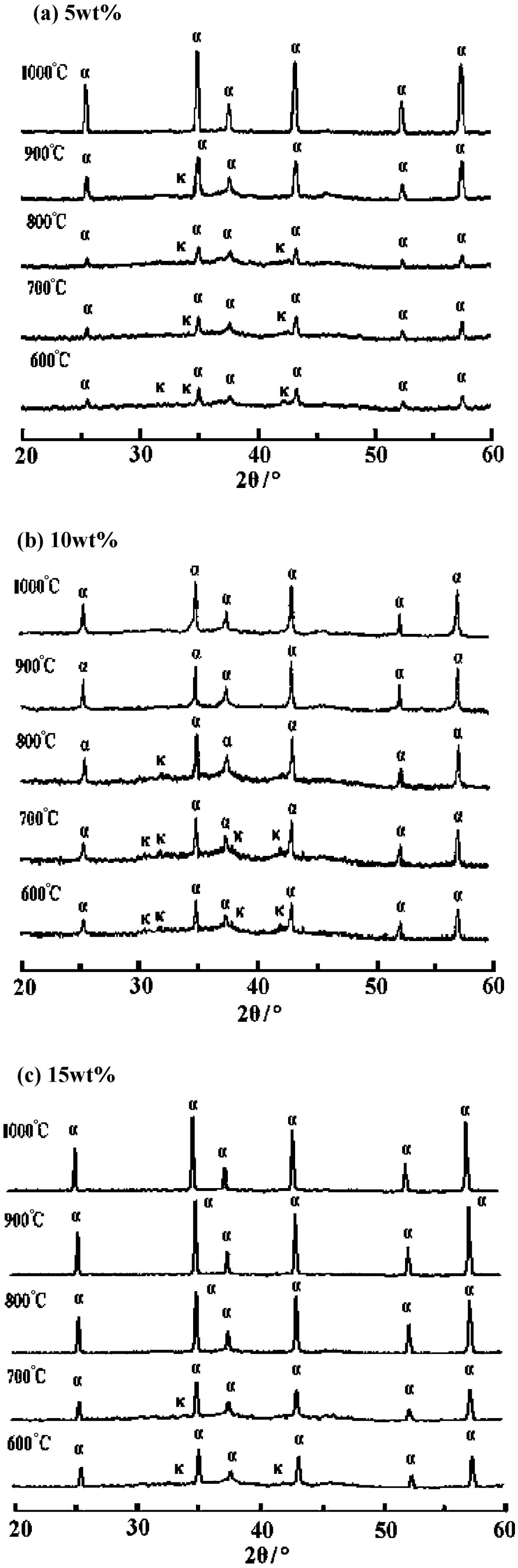

Figure 3 XRD patterns of aluminum hydroxide with various amounts of seed concentration calcined at 600–1000 °C for 4 hr in molten salt. (a) 5 wt%, (b) 10 wt% and (c) 15 wt%.

In conclusion, there are four intermediate phases, i.e. amorphous phase, κ-, δ- and θ-Al_2O_3 during calcining

$Al(OH)_3$ and single-phase α-Al_2O_3 finally forms at 1300 °C. When NaCl–KCl salt is added, only amorphous phase and κ-Al_2O_3 occur, and α-Al_2O_3 phase formation temperature decreases to 1100 °C. The addition of seeds further decreases the formation temperature, which is 1000, 900 and 800 °C for the samples with 5, 10 and 15 wt% α-Al_2O_3 seeds, respectively, in molten NaCl–KCl salt.

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