Advanced Powder Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Mechanically induced formation of metastable χ- and κ-Al_2O_3 from boehmite

Takahiro Kozawa *, Makio Naito

Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

ARTICLE INFO

Article history:
Received 21 August 2015
Received in revised form 15 February 2016
Accepted 18 February 2016
Available online xxxx

Keywords:
Boehmite
Gibbsite
Alumina
Phase transformation
Mechanical milling

ABSTRACT

Nanocrystalline boehmite (γ-AlOOH) powder was treated by high-energy planetary ball milling. With an increase in milling time and centrifugal force, boehmite was transformed into χ- and κ-Al_2O_3 as a metastable phase of alumina. These metastable alumina phases were confirmed by comparing with X-ray diffraction patterns of the thermally treated gibbsite (γ-$Al(OH)_3$). Eventually, the milling of boehmite resulted in the formation of thermodynamically stable α-Al_2O_3. Although boehmite is normally decomposed into γ-Al_2O_3 by heating, the phase transformation route of boehmite induced by mechanical milling differed from that induced by thermal process. We have proposed that the different phase transformation route can be attributed to the crystal deformation of boehmite by milling.

1. Introduction

Aluminum oxide (alumina, Al_2O_3) exists in many metastable phases besides the thermodynamically stable α-Al_2O_3. Valuable alumina polymorphs are commonly produced by heating of aluminum (oxy)hydroxide as a precursor [1]. One of their metastable alumina phases, γ-Al_2O_3, is widely used as a catalyst support from a perspective of high specific surface area and surface activity [2,3]. Usually, γ-Al_2O_3 powder is prepared by heating of γ-type aluminum oxyhydroxide (boehmite, γ-AlOOH) at around 500 °C. By the subsequent heat treatment, γ-Al_2O_3 undergoes a phase transformation into α-Al_2O_3 as follows [4]:

$$\gamma\text{-AlOOH} \rightarrow \gamma\text{-} \rightarrow \delta\text{-} \rightarrow \theta\text{-} \rightarrow \alpha\text{-}Al_2O_3 \tag{1}$$

With an increase in heating temperature, the phase transformation of boehmite occurs *via* metastable alumina phases until the formation of α-Al_2O_3 above 1100 °C. On the other hand, the formation process of metastable alumina phases depends on their precursors [1,5]. For instance, γ-type aluminum hydroxide (gibbsite, γ-$Al(OH)_3$) transforms into α-Al_2O_3 *via* another metastable phase during heating [6]:

$$\gamma\text{-}Al(OH)_3 \rightarrow \chi\text{-} \rightarrow \kappa\text{-} \rightarrow \alpha\text{-}Al_2O_3 \tag{2}$$

The difference in the formation process of α-Al_2O_3 is attributed to the crystal structure of precursors [7]. Accordingly, various alumina phases can be formed separately by tuning the heating temperatures and the starting precursors.

Besides the phase transformation induced by external heating, a mechanical approach using a high-energy milling apparatus has recently attracted attention because of a simple and low-cost process [8]. Mechanically induced phase transformation of γ-Al_2O_3 has been studied by many researchers [9–14]. Zieliński et al. [9] reported on the phase transformation of γ-Al_2O_3 into α-Al_2O_3 by a high-energy ball mill for 8 h. Kostić et al. [10] indicated that the transformation route of γ-Al_2O_3 by mechanical milling was identical with that by heating indicated in Eq. (1). However, An and co-workers [13,14] have reported on the contradictory results. The pure γ-Al_2O_3 showed a great stability on a high-energy ball mill and no phase transformation was observed after milling for 20 h [13]. Until now, a general consensus on the mechanically induced phase transformation of γ-Al_2O_3 has not been established yet.

Most of the thermally and mechanically induced phase transformations of alumina have used γ-Al_2O_3 as the stating material. Surprisingly, there have been few reports on the phase transformation of boehmite by mechanical treatment. Tonejc et al. [15–17] have performed the mechanical treatment of boehmite by using a planetary ball mill. They reported that boehmite was transformed into α-Al_2O_3 by milling for 2.5 h [15,16], and also suggested the transformation route *via* χ- and κ-Al_2O_3 as the intermediate phase [17]. This result disagrees with the phase transformation route presented in the heat treatment. Despite the different transformation route of boehmite induced by mechanical milling, it has

---

* Corresponding author. Tel.: +81 6 6879 4366.
E-mail address: t-kozawa@jwri.osaka-u.ac.jp (T. Kozawa).

http://dx.doi.org/10.1016/j.apt.2016.02.025
0921-8831/

Please cite this article in press as: T. Kozawa, M. Naito, Mechanically induced formation of metastable χ- and κ-Al_2O_3 from boehmite, Advanced Powder Technology (2016), http://dx.doi.org/10.1016/j.apt.2016.02.025

not been re-examined by other researchers. In the previous work by Tonejc et al. [17], however, the formed metastable phases were sufficiently indistinguishable by its low crystallinity and a contamination from milling media. The metastable χ- and κ-Al_2O_3 phases are useful materials as the catalyst support for CO conversion reactions [18,19] and the wear-resistant coating material on cemented carbide cutting tools [20], respectively. Therefore, the elucidation of the mechanically induced phase transformation behavior of boehmite leads to development of a new formation route of these metastable alumina phases. Thus, the objective of the present work was to clarify the transformation route of boehmite induced by mechanical treatment using a high-energy planetary ball mill.

2. Experimental

Commercially available boehmite powders (TAIMEI CHEMICALS Co., Ltd., Japan) were used in the present study. Fig. 1 shows the transmittance electron micrograph of the used boehmite. The plate-like crystals with the size of about 20 nm were observed. The crystallite size estimated by X-ray diffractometry and the equivalent particle size calculated by the specific surface area ($91.6\ m^2/g$) were 20 nm and 21 nm, respectively. These calculated particle sizes were in good agreement with the electron microscope observation. The mechanical treatment was carried out in a high-energy planetary ball mill (advanced type based on High-G BX254E, Kurimoto, Ltd., Japan) at room temperature using a stainless-steel pot ($V = 170\ cm^3$) and zirconia balls of 5 mm in diameter. The ratio of balls to boehmite powders was 90:1 by weight. By controlling a rotation speed of the revolution, the ball milling of powders was performed under three centrifugal forces of 50, 100, and 150 G. The boehmite powders were ball-milled at each centrifugal force for 1–12 h. The temperature rise of the pot after treatment was less than 50 °C. In order to compare the formed crystalline phases, the thermal treatment of gibbsite powder (Wako Pure Chemical Industries, Ltd., Japan) as well as boehmite powder was also examined in this study.

The crystalline phase of the products was identified by powder X-ray diffraction (XRD, D2 PHASER, Bruker AXS, Germany) using a Cu Kα-radiation at 30 kV–10 mA. The XRD patterns were recorded in the range of 10–90° in 2θ scanning mode with a 0.02° step and a scanning speed of 1.2°/min. The crystallite size was estimated by the Scherrer equation correcting the instrument peak width obtained from the (1 1 1) diffraction peak of Si powder (99.999% purity, Sigma–Aldrich, USA) added as an internal standard. Nitrogen adsorption measurements (3Flex, Micromeritics, Japan) in a relative pressure (P/P_0) range of 0.12–0.20 were performed to obtain the specific surface area (S_w). Prior to each measurement, the powder sample was outgassed under vacuum at 120 °C for 3 h. The S_w values were calculated by a 5-point BET method. The equivalent particle size (d_{BET}) was estimated from the specific surface area as follows: $d_{BET} = 6/(\rho \times S_w)$, where ρ is a theoretical density. The particle morphology was observed by transmittance electron microscopy (TEM, JEM-2010, JEOL Ltd., Japan). Diffuse reflectance Fourier transform-infrared (FT-IR, IRPrestige-21, SHIMADZU Co., Japan) spectra were measured on samples mixed with a dried KBr powder (MERCK kGaA, Germany).

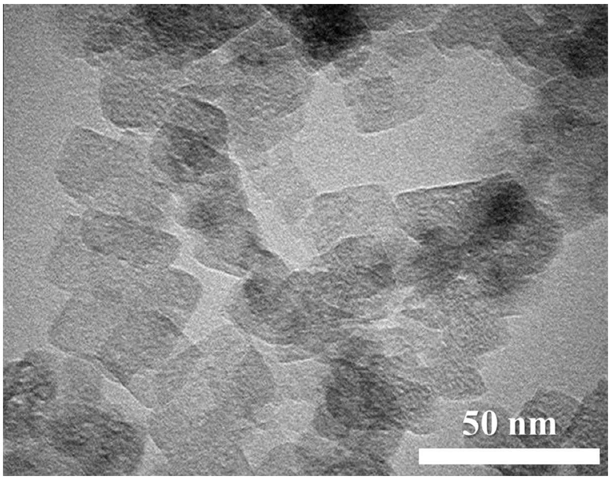

Fig. 1. TEM image of the used boehmite powder.

3. Results and discussion

Before milling experiments, we confirmed the phase transformation behavior of the used boehmite by heating at various temperatures for 2 h. The dehydration reaction of boehmite gradually occurred with an increase in heating temperature, and then γ-Al_2O_3 was obtained at 450 °C. The subsequent phase transformation of γ-Al_2O_3 was observed along the route indicated in Eq. (1). The complete transformation into α-Al_2O_3 was achieved by heating at 1300 °C.

Fig. 2 shows the XRD patterns of the boehmite powder after ball milling at a centrifugal force of 50 G and the products obtained by heating of boehmite and gibbsite. For the sake of simplicity, the mechanically treated samples are denoted the following as MT and the thermally treated samples as HT. In addition, the treatment condition is presented as time@centrifugal force or temperature in each figure. As shown in Fig. 2a, the XRD pattern of the MT boehmite at 50 G for 4 h was identical with that of the HT gibbsite at 500 °C. These products were attributed to a χ-Al_2O_3 phase. A clear

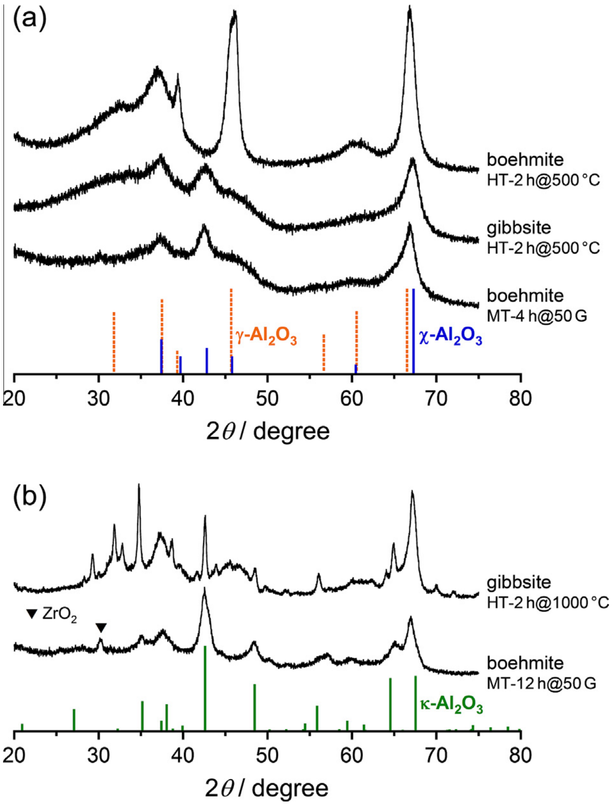

Fig. 2. XRD patterns of the mechanically (MT) and thermally (HT) treated boehmite and gibbsite powders: (a) MT boehmite at 50 G for 4 h and HT gibbsite and HT boehmite at 500 °C for 2 h; (b) MT boehmite at 50 G for 12 h and HT gibbsite at 1000 °C for 2 h. The standard XRD patterns of χ-Al_2O_3 and κ-Al_2O_3 are also shown.

Please cite this article in press as: T. Kozawa, M. Naito, Mechanically induced formation of metastable χ- and κ-Al_2O_3 from boehmite, Advanced Powder Technology (2016), http://dx.doi.org/10.1016/j.apt.2016.02.025