

EFFECT OF NH₄Cl ADDITIVES ON THE PHASE TRANSFORMATION AND MORPHOLOGY OF α -Al₂O₃

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Submitted December 2, 2022; accepted January 9, 2023

Keywords: α-Al₂O₃, NH₄Cl additive, Phase transition, Micromorphology

To investigate the effects of NH₄Cl doping and the calcination temperature on the phase transformation and microscopic morphology of Al_2O_3 , Al_2O_3 powders were obtained by introducing different mass fractions of NH₄Cl into the $Al(OH)_3$ powders and were then calcined at different temperatures. X-ray diffractometry and scanning electron microscopy were used for the phase analysis and particle morphology observation, respectively. The results showed that the addition of NH₄Cl could reduce the phase transition temperature of α - Al_2O_3 . With an increase in the NH₄Cl addition, the α - Al_2O_3 phase transition temperature significantly decreased. The transition phase was completely converted to α - Al_2O_3 at 1100 °C with the addition of NH₄Cl at 20 % at 1100 °C, which reduced both the phase transition temperature and the complete phase transition temperature of α - Al_2O_3 by 100 °C. Meanwhile, the introduction of NH₄Cl had no effect on the microscopic morphology of α - Al_2O_3 . The α - Al_2O_3 phases were worm-like with or without NH₄Cl, and the doping of NH₄Cl did not lead to the transitional growth of the complete phase-changed α - Al_2O_3 grains.

INTRODUCTION

Alumina is an important oxide with a broad range of promising applications in ceramics, glass, functional materials, adsorbents, catalysts and catalyst carriers. [1] The alumina crystalline phase include a variety of substable phases and thermodynamically stable α -Al₂O₃ or corundum. [2] At present, the common methods for preparing high-purity alumina powders are mainly the modified Bayer method, the thermal decomposition of aluminium hydroxide, the precipitation method and the hydrolysis of active high-purity aluminium, etc. All of these preparation methods are used to obtain the α -Al₂O₃ phase by the decomposition of aluminium hydroxide. [3] The transformation route of high temperature calcined aluminium hydroxide as follows: Al(OH)₃ \rightarrow AlOOH \rightarrow δ -Al₂O₃ is γ -Al₂O₃ \rightarrow θ -Al₂O₃ \rightarrow α -Al₂O₃ or Al(OH), $\rightarrow \chi$ -Al₂O₃ $\rightarrow \kappa$ -Al₂O₃ $\rightarrow \alpha$ -Al₂O₃ [4]. Transitions between sub-stable phases in the above transformation routes are caused by the local migration of aluminium ions and do not involve changes in the structure of the large skeleton of oxygen ions, the energy required in the phase transition is low, therefore, the phase transition can be completed at lower temperatures. [4, 5] However, the transition from the sub-stable phase to the α -Al₂O₃ phase is mainly due to the migration of oxygen ions. The arrangement of oxygen ions changing from the face-centred cubic (FCC) skeleton

to the hexagonal close-packed (HCP) skeleton, requires a higher energy, so the temperature in the transition from the sub-stable phase to the α -Al₂O₃ phase usually needs to be above 1200 °C. [6, 7] However, the high temperature transition usually leads to abnormal growth of the α -Al₂O₃ grains, resulting in a reduction in the properties of the α -Al₂O₃ phase. In order to obtain powder particles with smaller grains, it is necessary to reduce the temperature of the α -Al₂O₃ phase transition. According to the literature, [8-12] the transition temperature of the sub-stable phase to the α -Al₂O₃ phase can be reduced by adding α -Al₂O₃ crystalline seeds or additives, such as fluorides and chlorides, which are commonly used. After the addition of fluoride, the formation of gaseous transition phases such as HF. AlOF or AlF₃ with alumina raises the vapour pressure of the aluminium-containing material, which changes the formation of the α -Al₂O₃ phase from a solid-phase mode to a gas-phase transfer one, increasing the atomic diffusion rate and accelerating the phase transition process, thus reducing the transition temperature of the α -Al₂O₃ phase. [10, 13-15] It has been found that the introduction of chloride ions inhibits the growth of α -Al₂O₃ grains, and the commonly used chloride additives are NH₄Cl and MgCl₂. However, MgCl₂ would form an Mg-Al spinel heterogeneous phase while hindering the growth of the α -Al₂O₃ grains, making it difficult to generate high-purity α -Al₂O₃ powders. [16] In contrast, NH₄Cl decomposes at high temperatures and releases gas to produce shock effects, which improves the dispersion of the precursors. During this process, it does not generate a heterogeneous phase or lead to the transitional growth of grains, and there is no other heterogeneous phase generation. Researchers have found the influences of the NH4Cl addition on the phase transition temperature of α -Al₂O₃. However, there has been a lack of information on the optimal parametric amount and the mechanism of the effect of NH₄Cl on the crystalline transition of α -Al₂O₃ powders. Therefore, it is necessary to study the effect of chlorides on the phase transition temperature of α -Al₂O₃ and the reaction mechanism. In this paper, different levels of NH₄Cl were introduced into Al(OH)₃ powders, the effects of NH₄Cl on the phase transition temperature of α -Al₂O₃ and the morphology of the powder particles were investigated.

EXPERIMENTAL

The raw materials used in this study were a homemade aluminium hydroxide powder with a purity of > 99.999 % from the Fine Ceramics Centre of Dalian Jiaotong University, ammonium polyacrylate $(C_3H_7NO_2)$ and ammonium chloride $(NH_4Cl \ge 99.5 \%)$.

The aluminium hydroxide, ammonium polyacrylate and deionised water were mixed in mass ratios of 1:0.04:4 to form a 25 % aluminium hydroxide slurry, then different mass fractions of NH₄Cl were added to the slurry and ball-milled in a planetary ball mill for 4 h. The slurry was dried in a drying oven at a constant temperature of 60 °C. The powder was placed in a chamber electric furnace (SX-G01163) and heated to a predetermined temperature at a heating rate of 6 °C min⁻¹ and held for 1 h. To facilitate a comparison, samples of Al₂O₃ powder without NH₄Cl were prepared in the same way.

The phase evolution of the calcined samples was determined using an X-ray diffractometer (XRD, EMPYREAN, Netherlands) with a scanning speed of 4° min⁻¹ and a step size of 0.02° in the 2 θ range of $10^{\circ} - 90^{\circ}$ with CuK α radiation. The morphology of the prepared powder samples was observed using Scanning Electron Microscopy (SEM; SUPRA 55 SAPPHIRE, Germany).

RESULTS AND DISCUSSION

Figure 1 showed the XRD pattern of the sample without the additive after 1 h of calcination in the range of 800 °C – 1200 °C. The Al(OH)₃ and γ -Al₂O₃ diffraction peaks were present at 800 °C. As the temperature increased, the Al(OH)₃ diffraction peaks disappeared at 900 °C; while the γ -Al₂O₃ diffraction peaks gradually increased and the θ -Al₂O₃ diffraction peaks started

to appear. When the temperature was increased to 1000 °C, the θ -Al₂O₃ diffraction peaks gradually increased and the γ -Al₂O₃ diffraction peaks decreased, which indicated that γ -Al₂O₃ gradually transformed to θ -Al₂O₃. Between 900 °C and 1000 °C, the γ -Al₂O₃ phase and θ -Al₂O₃ phase coexisted. When the temperature increased to 1100 °C, α-Al₂O₃ diffraction peaks started to appear, while θ -Al₂O₃ diffraction peaks were still present. Until the temperature reached 1200 °C, the diffraction peaks of θ -Al₂O₃ disappeared completely, and only the diffraction peaks of α -Al₂O₃ existed in the diffraction pattern. This indicated that the sequence of phase transformation of this aluminium hydroxide without the additive during calcination was: γ -Al₂O₃ $\rightarrow \theta$ -Al₂O₃ $\rightarrow \alpha$ -Al₂O₃, and the formation temperature of α -Al₂O₃ is 1100 °C, and the complete phase transformation temperature is 1200 °C.



Figure 1. XRD patterns of the samples calcined at different temperatures without additives.

To investigate the effect of NH₄Cl additive on the phase transition of α -Al₂O₃, the samples were calcined at 1100 °C for 1 h after adding different mass ratios of NH₄Cl. The XRD results of the phase transition of the different samples were shown in Figure 2. From Figure 2, it could be seen that the θ -Al₂O₃ and a-Al₂O₃ phases also existed when the NH₄Cl contents were 10 - 18 %. However, the diffraction peaks of α -Al₂O₃ phase were more intense compared with that of the sample without the additive. Moreover, the diffraction peaks of θ -Al₂O₃ decreased gradually with the increase in the NH₄Cl contents, and when the addition of NH₄Cl reached 20 %, all the diffraction peaks of θ -Al₂O₃ disappeared and only the peaks of α -Al₂O₃ remained. This indicated that the addition of NH₄Cl lowered the complete phase transition temperature of α -Al₂O₃ by 100 °C compared with the sample without the additive.



Figure 2. XRD patterns of NH_4Cl at 1100 °C after calcination with the different additions.



Figure 3. XRD patterns after calcination at the different temperatures with the 20 % NH₄Cl additive.

To further verify the effect of the NH₄Cl addition on the phase transformation of α -Al₂O₃ at different temperatures, the samples with 20 % NH4Cl were calcined at 800 °C - 1300 °C for 1 h. The XRD patterns of the calcined samples were shown in Figure 3. The diffraction peaks of Al(OH)3 disappeared completely at 800 °C and θ -Al₂O₃ diffraction peaks started to appear, and the formation temperature of the θ -Al₂O₃ phase decreased by 100 °C compared with that of the sample without the NH₄Cl additive. As the temperature increased, the θ -Al₂O₃ diffraction peaks gradually increased and the γ -Al₂O₃ diffraction peaks decreased, indicating the transformation of the γ -Al₂O₃ phase to θ -Al₂O₃, which was consistent with the transformation pattern of the sample without the additives. As the temperature was further increased to 1000 °C, the α-Al₂O₃ phase started to precipitate at 1000 °C and completely transformed from the transition phase at 1100 °C. This lowered the formation temperature and complete transformation temperature of α -Al₂O₃ by 100 °C compared with that of the sample without the NH₄Cl additive.

In the absence of additives, the vapour pressure of alumina is relatively low and the transition from the transition phase to the α -Al₂O₃ phase is mainly by the solid-phase mass transfer. So, the transition from the transition phase to the α -Al₂O₃ phase is usually at a high temperature. When NH₄Cl is added to Al(OH)₃, the temperature of the α -Al₂O₃ phase transition is reduced. NH₄Cl decomposes at around 345 °C during calcination (Equation 1). [17] HCl (g) reacts with the sub-stable phase to form the gaseous intermediate product AlOCl (g), which is a highly unstable compound that can only exist at high temperatures and can easily decompose and transform into aluminium oxide and aluminium chloride (Equations 2 and 3). [19, 20]

$$NH_4Cl \to NH_3(g) + HCl(g)$$
 (1)

$$Al_2O_3(s) + 2HCl(g) \rightarrow 2AlOCl(g) + H_2O(g)$$
⁽²⁾

$$3AlOCl(g) \to AlCl_3(s) + Al_2O_3(s) \tag{3}$$

As NH₄Cl decomposes into NH₃ and HCl at high temperatures, it increases the vapour pressure in the furnace, which changes the formation of α -Al₂O₃ from a solid-phase mass transfer mode to a gas-phase mass transfer mode, accelerating the migration rate of the material and allowing alumina crystals to nucleate and grow rapidly. [17] Therefore, it promotes the transformation of the α -Al₂O₃ phase and lowers the temperature of the transformation of the sub-stable phase to the α -Al₂O₃ phase.

Morphological analysis

Figure 4 showed the SEM photographs after calcination at different temperatures with different additions of NH₄Cl. In Figure 4a of the sample without NH₄Cl, the powder morphology after calcination at 1100 °C showed both morphologies: elliptical and worm-like morphologies. When the calcination temperature was increased to 1200 °C, all the powders were worm-shaped (Figure 4b). The XRD results (Figure 1) showed that the θ -Al₂O₃ and α -Al₂O₃ phases existed in the sample without the additives at 1100 °C, and all the transition phases were transformed into an α -Al₂O₃ phase at 1200 °C. The worm-like morphology was typical of the necked growth of the α -Al₂O₃ phase. [20] It could be inferred that the particles with the elliptical form were the θ -Al₂O₃ phase. From Figure 4c, it could be found that the powders were all worm-like after calcination at 1100 °C in the sample with the 20 % NH₄Cl additive. Comparing Figure 4b and Figure 4c, the addition of 20 % NH₄Cl did not lead to an abnormal increase in the size of the full-phase transformed α -Al₂O₃ particles. This is due to the complete decomposition of NH₄Cl to NH₃ and HCl at around 345 °C, which improves the dispersion of the precursor and makes

the Al₂O₃ smaller in size during calcination. [17] The smaller particle size of Al₂O₃ particles can react with NH₄Cl more easily, so that the formation of α -Al₂O₃ phase changes mainly from a solid phase to mainly to a gas phase transfer, which accelerates the growth rate of α -Al₂O₃. Therefore, the addition of NH₄Cl cannot lead to an increase in the size of the α -Al₂O₃ particles.







Figure 4. SEM images of the NH₄Cl doping at the different temperatures after calcination: (a) 0 % at 1100 °C, (b) 0 % at 1200 °C, (c) 20 % at 1100 °C.



Figure 5. SEM images of the calcination with 20 % NH_4Cl at the different temperatures: (a) 800 °C, (b) 900 °C, (c) 1000 °C.

Figure 5 showed SEM photographs of the samples with the 20 % NH_4Cl additive after calcination at different temperatures. After calcination at 800 °C, the sample was irregularly flaky in shape (Figure 5a). As the calcination temperature increased, the flaky particles gradually dissolved into oval particles, and worm-like particles were found when the temperature

increased to 1000 °C (Figure 5c). According to Figure 4, it was found that the elliptical particles were the θ -Al₂O₃ phase, so the morphology of γ -Al₂O₃ was irregularly flaky, which was consistent with the reports of Peiris [21] and Sobhani [22] et al.

CONCLUSIONS

The experimental results showed that the introduction of NH₄Cl promoted the phase transition of α -Al₂O₃. When the addition of NH₄Cl was 20 %, the transition temperature and complete phase transition temperature of α -Al₂O₃ phase were both reduced by 100 °C. Simultaneously, the addition of NH₄Cl had no significant effect on the microscopic morphology of the α -Al₂O₃ phase, and the samples were in a worm-like form with or without the NH₄Cl addition. Moreover, the addition of NH₄Cl would not lead to the enlargement of the α -Al₂O₃ grains with the complete phase transformation.

Acknowledgments

The present work was supported by the Key R&D Program of Shandong Province (2019GSF109108) project.

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