Preparation of Micro/nano Sized Al₂O₃ Using the By-product of Al-based Composites Hydrolysis Reaction

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Abstract. In this paper, Al-based composites used for hydrogen production have been prepared by ball milling process. In order to reduce the cost of Al-based composites, we prepared micro/nano sized Al₂O₃ with the by-product of Al-based composites hydrolysis reaction. X-ray diffraction (XRD), scanning electron microscopy (SEM), and Mastersizer 2000 size analyzer are used for the analysis of the samples. The results show that Al₂O₃ phase is formed after the by-product milling for 4h and the by-product milled for 6h can reach micro/nanometer level. It is beneficial to reduce the cost of Al-based composites, which can promote the wide application of Al-based composites in the field of hydrogen production.

1. Introduction

Hydrogen is a clean and efficient energy source in the future energy supply. It is widely used as raw material for synthetic ammonia industry and hydrogen resources for proton exchange membrane fuel cell (PEMFC) [1-3]. Traditional methods to produce hydrogen include steam reforming and water electrolysis. Nowadays, there are many new ways for hydrogen production, such as bio-hydrogen production, solar hydrogen production and Aluminum (Al) hydrolysis hydrogen production [4]. However, there are more or less problems when we apply these methods to produce hydrogen, including inefficiency, fossil fuel consumption, and high cost. Hydrogen production using Al and Al-based composites is considered as a promising way to solve those problems [5]. As we all know, other additives are usually added into the Al to remove the dense passive layer formed on its surface, which prevents the hydrolysis reaction between Al and water at room temperature. However, the price of Al-based composites with other additives would increase, leading to this hydrogen production method lying in the laboratory.

It is well known that the chemical reactions of Al with water is as Eq. (1):

\[ Al + H_2O \rightarrow Al(OH)_3/AIOOH + H_2 \]  

(1)

According to Reference [6] and [7], We prepare Al-8wt%Bi-7wt%NaCl composites for hydrogen production, and then prepare micro/nano sized Al₂O₃ with its hydrolysis by-product.

2. Experimental
2.1. Preparation of Al-based composites used for hydrogen production

Aluminum (99.0%, 100-200 mesh), Bi (99.9%, ≥200 mesh), and NaCl (99.5%, AR) were used as received. The Al-8wt%Bi-7wt%NaCl composites weighed and placed into alumina pots in an argon-filled glove box were prepared by a planetary ball miller (QM-3SP04) at a ball-to-powder mass ratio of 15:1 and 420 rpm for 360 min. The hydrolysis reaction of Al-8wt%Bi-7wt%NaCl composites with tap water was carried out in a beaker containing. 10g Al-8wt%Bi-7wt%NaCl composites were placed into a 1000-mL beaker containing (500 mL) tap water, and then the 1000-mL beaker was put in a constant temperature water bath (50°C). After that, the raw materials prepared for micro/nano sized Al₂O₃ were gained by precipitation filtration.

2.2. Preparation of micro/nano sized Al₂O₃

The by-production of Al-water reaction was used as starting materials for micro/nano sized Al₂O₃ preparation. Micro/nano sized Al₂O₃ were prepared with a planetary ball miller (QM-3SP04) at a ball-to-powder mass ratio of 15:1 and 420 rpm for different milling time (0.5-48h). Then, the materials were dried for 12h in a blast oven at 110 °C. The phase compositions of the by-product and micro/nano sized Al₂O₃ were characterized by X-ray diffraction (XRD) with Cu kα radiation. The surface morphology analyses for all the samples were performed using scanning electron microscopy (SEM). The particle size was measured by Mastersizer 2000 Size Analyzer.

3. Results and discussion

3.1. The phase compositions of the by-product

Fig.1 shows the XRD pattern of the by-product of Al-8wt%Bi-7wt%NaCl hydrolysis reaction. It reveals that the presence of Al(OH)₃ and AlOOH in the by-product. This result is similar to those reported in Reference [7]. However, no obvious peaks of Bi or its alloys were observed in by-product XRD pattern, which may be due to its low content.

![Fig.1 XRD pattern of the by-product of Al-8wt%Bi-7wt%NaCl hydrolysis reaction](image)

3.2. The surface morphology of the by-product

Fig.2 shows the SEM images of the by-product of Al-8wt%Bi-7wt%NaCl hydrolysis reaction. It suggests that the by-product is in flower clusters, which could use to prepare micro/nano sized Al₂O₃ by change of phase compositions and particle size with ball milling.
3.3. The phase compositions of the by-product milled with different milling time

Fig. 3 presents XRD pattern of the by-product of Al-8wt%Bi-7wt%NaCl hydrolysis reaction milled with different milling time. The results show that the AlOOH and Al(OH)₃ phase disappear gradually, whereas Al₂O₃ phase is formed during the prolonged ball milling time. Therefore, it could be inferred that two chemical reactions took place during the ball milling process as follows (Eq. (2) and (3)):

\[
2\text{Al(OH)}_3 \xrightarrow{\text{ball milling}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \tag{2}
\]

\[
2\text{AlOOH} \xrightarrow{\text{ball milling}} \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \tag{3}
\]

The formation of Al₂O₃ may be caused by the collision between by-product and ball and consequently chemical reactions shown above were happened under mechanical force loading during the ball milling process. Fig. 3 shows that new products were Al₂O₃ except a small amount of Al(OH)₃ after ball milling for 4h. Furthermore, all of the new products are Al₂O₃ when the milling time reached 24h.

3.4. The particle size of Al₂O₃ prepared by the by-product

The particle size distribution of by-product milled with different time has been illustrated in Fig. 4, demonstrating that the particle size distributions changed significantly with the increase of milling time. The particle size distribution of unmilled by-products ranges from 3 to 110µm, of which the particle size D50 is 28.8µm. Its particle size distribution is wider than other milled samples. The particle size of milled by-products first decreases and then increase. The particle size distribution of 6h milled by-products ranges from 0.2 to 8µm, of which the particle size D50 is 0.94µm. The results show that the by-product of Al-8wt%Bi-7wt%NaCl composites hydrolysis reaction milled with 6h can reach micro/nanometer level. However, the particle size distribution of 48h milled by-products ranges.
from 0.2 to 70μm, of which the particle size D50 is 1.74μm. Apparently, the particle size increases and then reached its limit with the prolonged milling time.

Fig.4 The particle size distribution curves of by-product milled with different time

4. Conclusions
In summary, Al-8wt%Bi-7wt%NaCl composites and micro/nano sized Al2O3 were prepared by ball milling, and its phase composition, morphologies, and particle size distribution were investigated. The results show that the by-product of Al-8wt%Bi-7wt%NaCl composites hydrolysis reaction milled with 6h can reach micro/nanometer level. It is beneficial to the subsequent processing of the micro/nano sized Al2O3 and to reduce the cost of Al-based composites in the field of hydrogen production.

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