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Formation of Bi-Li Alloy and its Mechanism to Improve the Hydrolysis Kinetics of Aluminum

Wei Xia[1], Zhujian Li[1], Haifei Long[1], Jindan Chen[1], Ting Li[1], Mei Qiang Fan[*,1] and Yong Jin Zou[2]

[1]Department of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, P R China
[2]Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, P.R. China

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Abstract: *The formation of Bi-Li alloy and its potential mechanism to improve the hydrolysis kinetics of Al had been presented in the paper. Bi-Li alloy could exist steadily and deposited on Al surface uniformly from XRD and SEM-EDX results because Bi-Li alloy had low melting temperature. The formation of Al- $BiLi_3$ microstructure created active sites which produced galvanic micro cell of Al and Bi in the hydrolysis process. Therefore, hydrolysis performance of Al- $BiLi_3$ composites was significantly improved with $BiLi_3$ content increasing.*

Keywords: $BiLi_3$ alloy; hydrolysis; active sites

1. INTRODUCTION

Aluminum is a potential hydrogen source for micro proton exchange membrane fuel cell. It has many attractive advantages such as low cost, mild hydrolysis conditions, hydrogen purity, etc. However, aluminum can not react with pure water at room temperature due to the formation of alumina on aluminum surface and its hydrolysis byproduct prevents the continuous hydrolysis of aluminum. Many methods have been introduced to improve aluminum activity in the past ten years [1, 2]. Using alkali solution is a common method to accelerate the hydrolysis of aluminum. The alkali acts as a catalyst and alkali species and their concentrations have great effect on hydrolysis kinetics of aluminum and water [3]. It is a pity that the alkali is not easily handled and may have some damages for common users in the actual application. Doping some additives to aluminum and even forming aluminum alloys may also improve aluminum activity in pure water at room temperature. The additives include metals (Bi, Zn, Sn, In, etc), oxides (Al_2O_3, TiO_2, etc) and salts (NaCl, $CoCl_2$, $NaSnO_3$, etc) [4-8]. The composite of aluminum and additives had almost 100% of hydrogen yield at room temperature. The activation mechanisms had been elaborated as the formation of nanometer particles in the preparation process and galvanic micro cell in water. The sustainable researches are performed to optimize the aluminum composite with high theoretical hydrogen generation amount and rate as the additives often do not react with water.

In our recent work, the aluminum doped with Bi and Li had fast hydrogen generation rate and amount at room temperature [9]. Sometimes, the aluminum composites with high Li content even fired in water because the reaction of Li and water released a lot of heat. There existed some intermetallic compounds of Li and Bi in the Al composite and the hydrolysis performance improvement of Al might come from the synergistic effect of Li and Bi on the hydrolysis of aluminum as the hydrolysis byproduct LiOH stimulated the galvanic micro cell of Al and Bi. However, the detailed potential effect of Bi-Li alloy was not elaborated because there were some AlLi alloys in Al composites. In addition, the hydrolysis byproduct LiOH presented alkali which also acted as a catalyst for Al hydrolysis. So far, the potential mechanism of Bi-Li alloy had been not explained detailedly.

Therefore, in the paper, the BiL_3 were formed and then the composite of Al and BiL_3 were obtained via milling method. The microstructure and hydrolysis properties were performed to elaborate the effect of $BiLi_3$. The potential mechanism was helpful to optimize aluminum composite.

2. EXPERIMENTAL

2.1. Sample preparation

Aluminum powder (99.9% purity, ~10 μm particle size; Beijing Xingry Technology Company, Ltd., China), Li flakes (99.9% purity; China Energy Lithium Co., Ltd., China), pure Bi powder

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*To whom correspondence should be addressed: Email: fanmeiqiang@126.com
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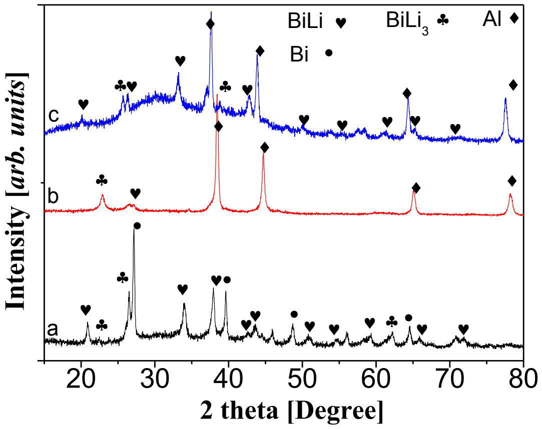


Figure 1. XRD patterns of BiLi$_3$ (a), Al-10 wt% BiLi$_3$ (b) and Al-20 wt% BiLi$_3$ (c).

(Beijing Xingry Technology Company, Ltd China) were used as starting materials. All reagents were used as received. The reagents were weighed and placed in 50 mL stainless steel jars to which stainless steel balls were added. The jars were kept in an argon-filled glove box. The ball-to-mixture weight ratio was 26 to 1. Milling for 10 h was done in a QM-3SPO4 planetary ball miller at 450 r/min and a 0.2 MPa argon atmosphere, unless otherwise indicated. The BiL$_3$ were prepared firstly and then the composite of Al and BiL$_3$ was further obtained using the milling method.

2.2. Measurement of hydrolysis kinetics

The hydrolysis experiments were performed in a sealed reactor attached a condenser and a graduated cylinder at 25 ^{0}C and 1atm. The detailed hydrolysis conditions were similar to those in our pervious works [9]. The hydrolysis experiments at 30, 40, 50 and 60 ^{o}C were carried out. The activation energy was calculated according to the Arrhenius equation:

$$k = A \cdot \exp\left(-E_a / RT\right) \qquad (1)$$

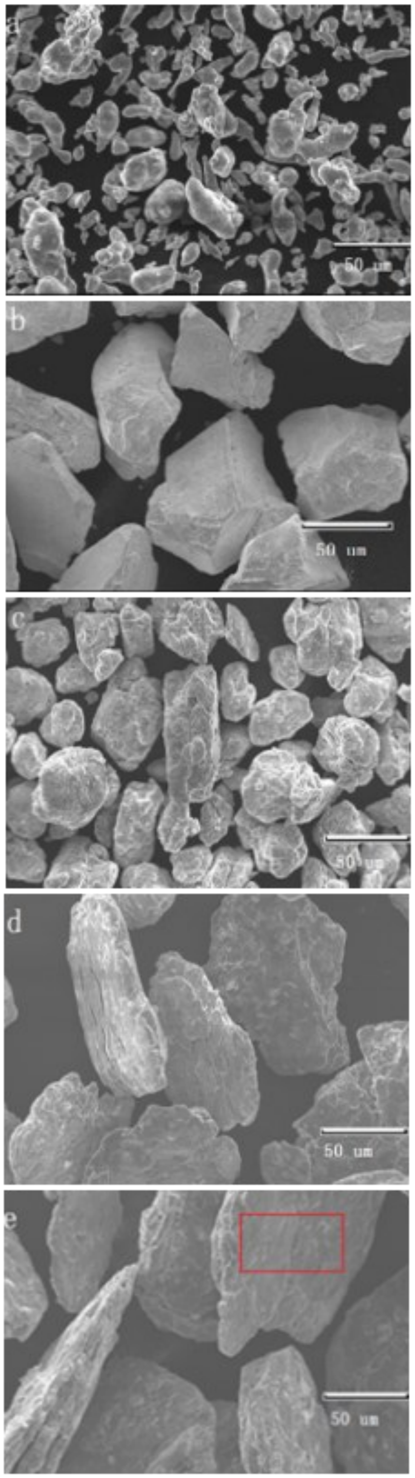
In the equation, K is a rate constant and T is the hydrolysis temperature and Ea is the activation energy. the apparent activation energy is collected by a linear regression of ln (k) versus 1000/T with a good fitting, based on reaction (1).

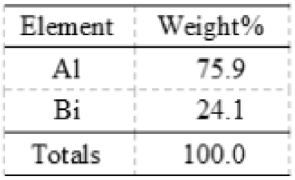
2.3. Microstructure analysis

Powder X-ray diffraction (XRD) patterns of the prepared samples were obtained on an X-ray diffractometer (Thermo ARL X’TRA Switzerland,). Scanning electron microscopy (SEM) observations were performed using a JSM-5610LV (JEOL Co.) equipped with an INCA energy-dispersive X-ray spectrometer.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of milled Bi-Li and Al-Bi-Li composites. The peaks of BiLi and BiLi$_3$ were identified from the XRD patterns of milled Bi-Li composite, showing that Bi metal combined with Li metal in the milling process. The peaks of BiLi and BiLi$_3$ except those of Al were also identified from the XRD patterns of milled Al-10wt% BiLi$_3$ and Al-20 wt% BiLi$_3$ composites,





Element	Weight%
Al	75.9
Bi	24.1
Totals	100.0

Figure 2. SEM of Al (a), Bi (b), BiLi$_3$ (c), Al-10 wt% BiLi$_3$ (d) and Al-20 wt% BiLi$_3$ (e).

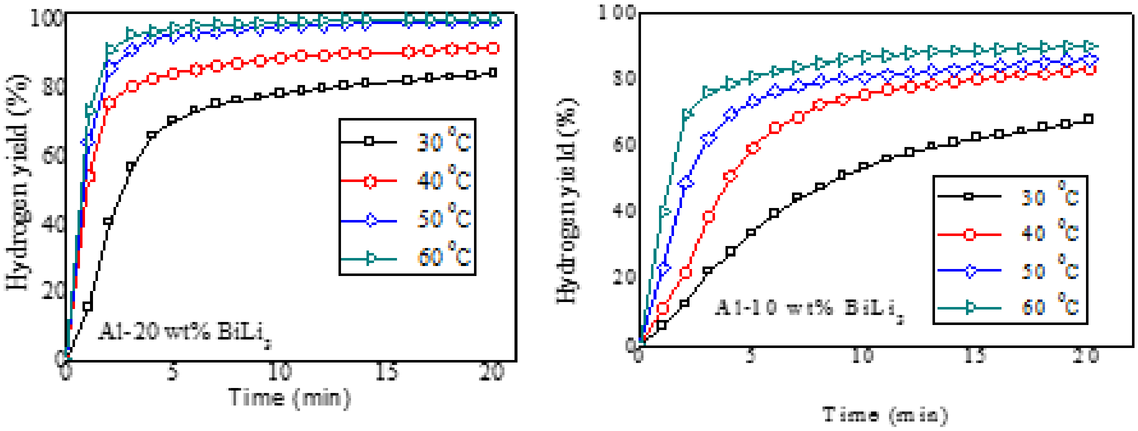


Figure 3. Hydrogen generation of Al-BiLi$_3$ composites at different temperature.

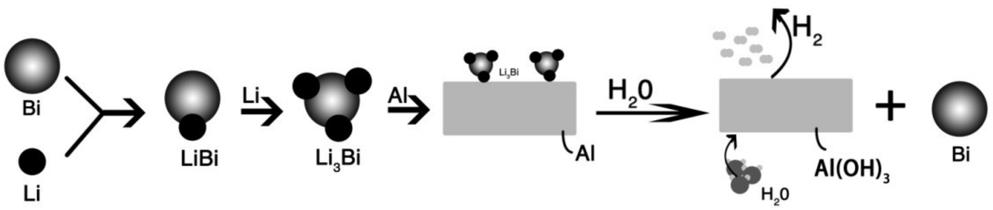


Figure 4. Schematic activation and hydrolysis mechanism of Al-BiLi$_3$ composites

exhibiting that BiLi and BiLi$_3$ could be stable in the milled Al-BiLi$_3$ composites. But the peaks of Bi disappeared and the peaks of Al shifted to low degrees with BiLi$_3$ content increasing from 10 wt% to 20 wt%. Bi metal has low melting temperature and nanometer Bi particle deposited on Al surface and dissolved into Al matrix with long milling time. The similar phenomenon would be easier for BiLi$_3$ because it has lower melting temperature than that of Bi and Li metal has high ability to combine with Al. More strains and defects occurred in the milled Al-BiLi$_3$ composites with high BiLi$_3$ content, resulting in the peaks shift of Al.

Figure 2 shows SEM of Al, Bi, BiLi$_3$ and Al-BiLi$_3$ composites. Pure Al and Bi powder has about 10 and 50 um of particle size, respectively. Al powder presents columnar and Bi powder has irregular shape. Milled BiLi$_3$ alloy had smaller particle size than that of Bi. Its particle size ranged in 10～50 um. Lots of defects occurred on particle surface and particle shape became flat. The trend was further significant in milled Al-BiLi$_3$ composites. Large flats were observed with approximate 50 um of particle size and about 10 um of thickness. Al metal has good ductility and its shape evolve gradually from columnar to flat in the milling process. In the evolution process, BiLi$_3$ alloy deposited on Al surface uniformly as it has low melting process.

The EDS of small area in Figure 2e shows that weight ratio of Al and Bi is up to 75.9% and 24.1%, respectively. Therefore, the formation of Al- BiLi$_3$ composites could be elaborated that Bi metal combined with Li metal firstly to form BiLi$_3$ alloy and then BiLi$_3$ alloy distributed into Al surface. Potential galvanic cell between Al and BiLi$_3$ occurs and acts as the active sites when Al-BiLi$_3$ composites contact with water.

Figure 3 shows hydrogen generation of Al-BiLi$_3$ composites at 30, 40 ,50 and 60 ^{o}C. The hydrogen generation rate is affected by composite design and hydrolysis temperature. Al-20 wt% BiLi$_3$ composite has better hydrolysis performance than that of Al-10 wt% BiLi$_3$ composite at the same conditions, showing that the addition of BiLi$_3$ is an important factor for Al hydrolysis. At 30 ^{0}C, the hydrogen yield of Al-10 wt% BiLi$_3$ and Al-20 wt% BiLi$_3$ composite was up to 67 and 84 % in 20 min, respectively. At 40 ^{0}C, the hydrogen yield of Al-10 wt% BiLi$_3$ and Al-20 wt% BiLi$_3$ composite was increased to 83 and 92% at the same conditions. With temperature increasing to 50 ^{0}C, hydrogen yield of the composites continued to be increased to approximate 100%. The activation energy of the Al-BiLi$_3$ composite could be calculated according to Soler's method [10]. The result of 39 and 16 kJ/mol was corresponded to Al-10 wt% BiLi$_3$ and Al-20 wt% BiLi$_3$ composite, respectively.

The addition of BiLi$_3$ improved the hydrolysis performance of Al. The potential mechanism can be elaborated in the following. The particle size of milled Al - BiLi$_3$ did not decrease in the milling process but the particle shape became from sphere to flat. The BiLi$_3$ alloy existed steadily and distributed into Al matrix uniformly from the results of XRD and EDX because BiLi$_3$ had lower melting temperature than that of Bi. Many potential Al- BiLi$_3$ active sites occurred and formed galvanic micro cell of Al and Bi in the hydrolysis process. The detailed formation of BiLi$_3$ and its potential mechanism had been described in Figure 4. The effect of Li hydrolysis had not been considered as it has very low concentration in the design of the Al- BiLi$_3$ composite.

4. CONCLUSION

The hydrolysis performance of Al- 10 wt% $BiLi_3$ and Al- 20 wt% $BiLi_3$ composites had been presented in the paper. Al- 20 wt% $BiLi_3$ composite had higher hydrogen yield than that of Al- 10 wt% $BiLi_3$ composite in 20 min of hydrolysis. From the results of XRD and SEM-EDX, the hydrolysis performance improvement of Al-$BiLi_3$ composite came from that $BiLi_3$ distributed into Al matrix uniformly and created Al- $BiLi_3$ active sites. The active sites formed galvanic micro cell of Al and Bi and accelerated the hydrolysis of Al. Therefore, how to obtain more and more active sites on Al surface maybe an important factor to design highly active Al powder.

5. ACKNOWLEDGMENTS

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