Enhanced Hydrolysis Performance of Al-Li-Ni$_3$Sn$_2$ Composites for Hydrogen Generation and Relative Mechanism

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Abstract: *The Al-Li-Ni$_3$Sn$_2$ composites were prepared via milling method and their hydrolysis performance was presented in the paper. The milled Al-Li-Ni$_3$Sn$_2$ composites showed high hydrolysis performance at 30-60^{0}C, especially that Al-3.5wt%Li-20wt%Ni$_3$Sn$_2$ composite had 100% and 1103 ml hydrogen/g of hydrogen yield within 20 min at 50^{0}C.The hydrolysis performance improvement of Al-Li-Ni$_3$Sn$_2$ composite was due to the addition of Ni$_3$Sn$_2$ while Ni$_3$Sn$_2$ combined with Al and formed nano structure of Ni-based alloys deposited on the surface of Al. The structure of Al-(Ni alloy) could act as active sites in the hydrolysis process because the milled products such as AlNi, Al-NiSn and Al- Ni$_3$Sn$_2$ had high electrochemical activity in the hydrolysis process. Therefore, Al-Li-Ni$_3$Sn$_2$ composites were a potential hydrogen source for fuel cell.*

1. INTRODUCTION

Aluminum is a good hydrogen source for micro fuel cell because it has low cost, highly theoretic hydrogen yields and mild hydrolysis condition, etc. Aluminum can be easily used for large-scale hydrogen production as it has mature industry manufacture technology. Aluminum is easily oxidized to be alumina or aluminum hydroxide which can be recycled. However, the dense layer of alumina or aluminum hydroxide on aluminum surface often prevents the continuous hydrolysis of aluminum. To resolve the above problem, many methods including alkaline solution [1], alloying [2, 3], doping metal oxides [4], etc, have been developed to accelerate the hydrolysis of aluminum in the past ten years. The designed composite of aluminum and additives had improved hydrogen yield in comparison with pure aluminum at mild conditions.

Alloying has been availably developed to enhance the activity of aluminum in pure water. Scientists [5, 6] prepared the aluminum alloys including low melting point metals such as Bi,Ga,In, Sn,Zn, etc. The aluminum alloys had high hydrolysis activity under mild conditions. O.V. Kravchenko et al [6] obtained aluminum alloys with Ga, Sn, In, Zn metal by melting method. The optimized alu-

minum alloy with 20 wt% other metals achieved 1060 ml hydrogen/g at 25^{0}C. Parmuzina et al [7] used liquid eutectic Ga-Sn or Ga-Zn-In-Sn as the additives to activated aluminum powder. The milled aluminum alloy powder had high hydrogen yield up to 99% of theoretical value. The eutectic alloys formed on the aluminum surface were considered to be responsible for the activity enhancement of aluminum. In our precious work, the hydrolysis performance improvement of Al was further elaborated as the micro galvanic cell between Al and other metals [8]. Therefore, the potential intermetallic compounds and its uniform deposition on aluminum surface are key important to improve the activity of aluminum.

In the presented paper, the initial Ni$_3$Sn$_2$ alloy were used and deposited on aluminum surface via the milling method. The microstructure and hydrolysis properties were performed to optimize aluminum composite and elaborate the effect of Ni$_3$Sn$_2$. A little lithium metal was added as Li metal can greatly simulate the hydrogen generation rate of aluminum [9].

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% puri-

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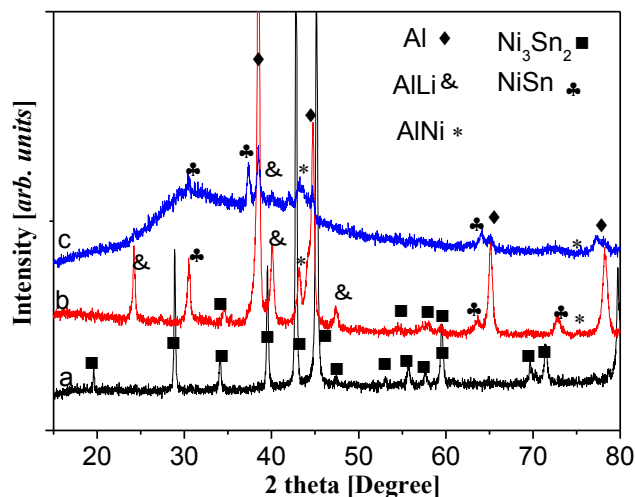Phone:

Figure 1. XRD patterns of Al-Li-Ni$_3$Sn$_2$ composites.

Figure 2. SEM images of Al (a), Ni$_3$Sn$_2$; (b), Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$; (c) and Al-3.5 wt%Li-20 wt%Ni$_3$Sn$_2$ (d).

ty; China Energy Lithium Co., Ltd., China), Ni$_3$Sn$_2$ alloy powder were used as starting materials. 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 Ni$_3$Sn$_2$ alloy powder was prepared via melting method shown in our previous work [10].

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:

$$k = A \cdot \exp(-E_a / RT) \tag{1}$$

Here, 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

3.1. Microstructure analysis

Fig.1 shows XRD patterns of Al-Li-Ni$_3$Sn$_2$ composites. All the diffraction peaks were identified as those of the Ni$_3$Sn$_2$ (Orthorhombic, Pnma) single-phase powder preparation. But the
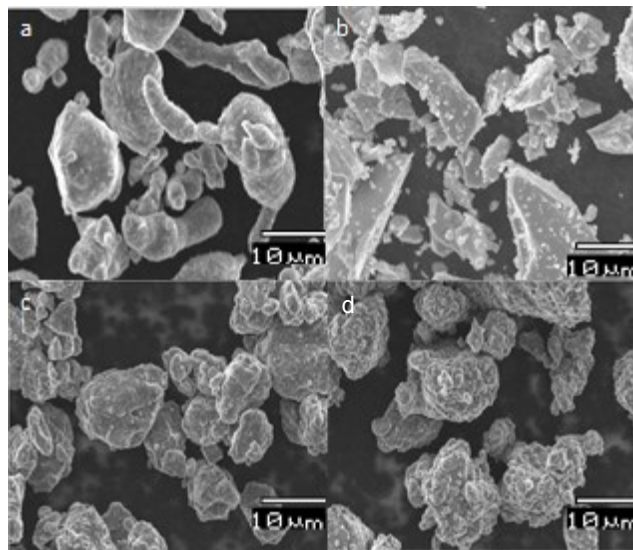
peaks of Ni$_3$Sn$_2$ at 19.8^0, 29.2^0, 42.7^0 and 45.0^0 disappeared in the XRD patterns of Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$ composite. New peaks of AlLi, AlNi and NiSn were demonstrated except those of Al and Ni$_3$Sn$_2$, suggesting that the reactions between Al, Li and Ni$_3$Sn$_2$ occurred in the milling process, as shown in equations (2) and (3).

$$Al+Li \rightarrow AlLi \tag{2}$$

$$Al+ Ni_3Sn_2 \rightarrow AlNi+NiSn \tag{3}$$

The peaks of Al, AlLi, AlNi and Ni$_3$Sn$_2$ presented broad, reflecting that the milled Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$ composite had small particle size. It could be explained that the composite experienced repeated welding, fracturing and rewelding in the milling process, where many defects and deformations were generated and strengthened due to the formation of intermetallic compounds [11]. Therefore, the peaks line became wider in the XRD patterns of Al-3.5 wt%Li-20 wt%Ni$_3$Sn$_2$ composite, including peaks for Al, AlNi and NiSn. The results showed that the particle size of the milled Al-3.5 wt%Li-20 wt%Ni$_3$Sn$_2$ composite significantly decreased in comparison with that of the milled Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$ composite. Some peaks for AlLi and Ni$_3$Sn$_2$ even disappeared and a big wide peak in the range of 20-30^0 occurred correspondingly. The change was related to the addition of Ni$_3$Sn$_2$ alloy. Ni$_3$Sn$_2$ alloy powder presented brittle and easily ruptured in the milling process. The fine Ni$_3$Sn$_2$ distributed on the surface of Al and reacted with aluminum particle. So the recombination of Al and Al was interrupted and fine Al particle was generated thereby. The Ni$_3$Sn$_2$ concentration increase of Al-Li-Ni$_3$Sn$_2$ composite was helpful to broaden the peaks line of in the XRD patterns, especially that the big wide peak line exhibited nanostructure generated in the milling process.

Fig.2 shows morphology of Al and Al-Li-Ni$_3$Sn$_2$ composite. Al powder with approximate ten um diameter presented columnar and
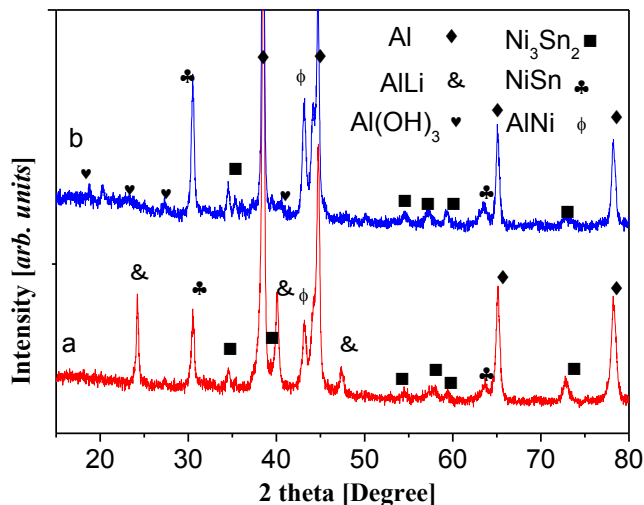
Figure 3. XRD patterns of Al-3.5wt% Li-10 wt% Ni$_3$Sn$_2$ composites before (a) and after hydrolysis (b) at 30^{0}C.

had relatively smooth surface. The Ni$_3$Sn$_2$ alloy powder had different particle size ranging in several hundreds of nm – ten of um. Some large particles showed relatively smooth surfaces with a few small particles. The particles had several hundreds of nm in diameter. After milled together, the Al-Li-Ni$_3$Sn$_2$ composite exhibited different morphology. Lots of defects and deformation were observed. The composite presented irregular flat and lots of fine particles piled up together. The fine particles had several um in diameter. There were also some differences between Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$ and Al-3.5 wt%Li-20 wt%Ni$_3$Sn$_2$. Some flats and fine particles piled up were observed on the surface of Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$ composite. Little flats but lots of fine particles piled up were observed on the surface of Al-3.5 wt%Li-20 wt%Ni$_3$Sn$_2$ composite. The flat was generated due to the welding, fracturing and rewelding in mechanical milling. The fine particles piled up might be explained as the reaction product of Al and Ni$_3$Sn$_2$ alloy. The trend from flat to fine particle piled up occurred with the increase of Ni$_3$Sn$_2$ alloy.

Fig.3 shows XRD patterns of Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$ composite before and after hydrolysis at 30 ^{0}C. The peaks of Al, AlLi, NiSn, Ni$_3$Sn$_2$ and AlNi were demonstrated in the XRD patterns of Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$ composite. After hydrolysis at 30 ^{0}C, the peaks of AlLi disappeared and new peaks of Al(OH)$_3$ occurred except the peaks of Al, AlNi and NiSn. The peaks line of NiSn and Ni$_3$Sn$_2$ became stronger in comparison with the weaker those of Al. The results showed that the Al or AlLi in the composite could hydrolyze at mild temperature, but NiSn, Ni$_3$Sn$_2$ remained after the hydrolysis process.

3.2. Hydrogen generation performance

Fig.4 shows hydrogen generation performance of Al-Li-Ni$_3$Sn$_2$ composites at 50^{0}C. Al-10wt%Li alloy had bad hydrogen generation performance at 50 ^{0}C, with approximate below 60% hydrogen yield. Lithium metal was active in pure water and the hydrolysis product LiOH was a catalyst for the hydrolysis of Al. But low Li concentration in Al-Li alloy led to low LiOH amount which could
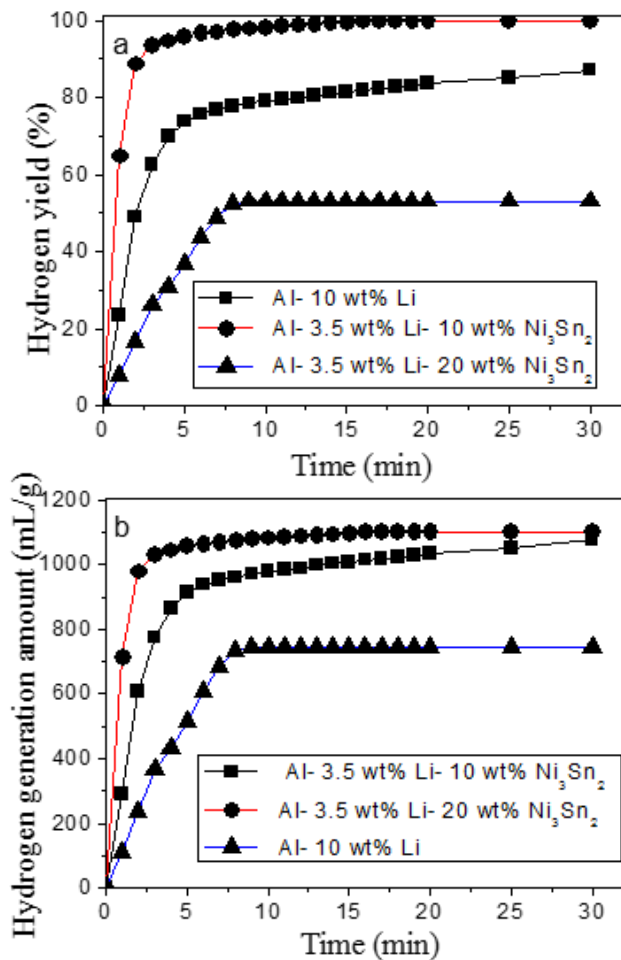

Figure 4. Hydrogen generation performance of Al-Li-Ni$_3$Sn$_2$ composites at 50 ^{0}C.

not improve the hydrolysis of Al completely. Actually, Al-3.5 wt%Li alloy almost had not collected measured hydrogen in our experiments. However, Al-3.5wt%Li-10wt%Ni$_3$Sn$_2$ composite had improved hydrolysis performance at the similar conditions, with 85% of hydrogen yield. With Ni$_3$Sn$_2$ concentration increasing to 20 wt%, the composite had almost 100% of hydrogen yield. In comparison with low hydrolysis kinetics of Al-10 wt%Li alloy, Al-Li-Ni$_3$Sn$_2$ composites had significant improved hydrogen generation rates. Al-3.5wt%Li-10 wt%Ni$_3$Sn$_2$ composite could achieve 70% of hydrogen yield below 3 minutes and Al-3.5wt%Li-20 wt%Ni$_3$Sn$_2$ composite reached 90 % hydrogen yield in 2 minutes. The Al-Li-Ni$_3$Sn$_2$ composites had slow hydrogen generation rate after the quickly initial hydrolysis in the first several minutes. There was an inflection in the hydrogen generation curves and the time for the inflection was inversely proportional to Ni$_3$Sn$_2$ concentration in the composite. The hydrogen generation curves could be divided to two periods from the inflection: the quick hydrogen generation period and the slow hydrogen generation period, the quick hydrogen generation period were seriously affected by the Ni$_3$Sn$_2$ concentration in the composite. Higher hydrogen yield of this period was proportional to Ni$_3$Sn$_2$ concentration. The slow hydrogen gen-

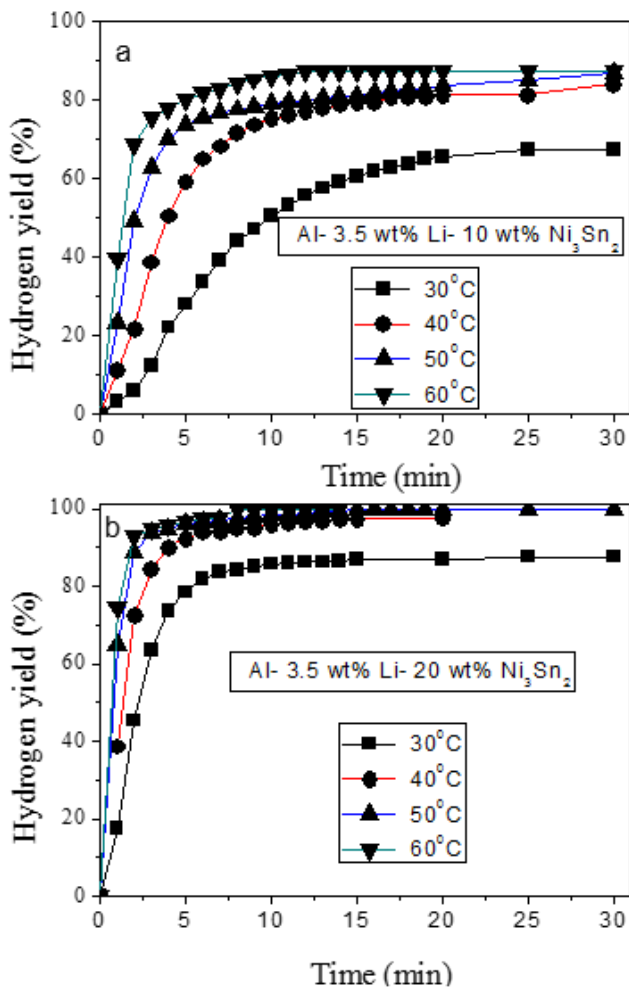Figure 6. Hydrogen generation amount of Al-Li-Ni$_3$Sn$_2$ composites at different temperature.

Figure 5. Hydrogen generation performance of Al-Li-Ni$_3$Sn$_2$ composites at different temperature.

eration period was also a little affected by the Ni$_3$Sn$_2$ concentration in the composite, but its change trend was not similar to that of the quick hydrogen generation period.

The detailed relationship between hydrogen generation amount and hydrolysis time is shown at Fig.4b. Al-10wt% Li could only produce 743 ml hydrogen/g before 7 min and did not generate hydrogen in the followed hydrolysis time. Al-3.5wt%Li-10 wt%Ni$_3$Sn$_2$ composite generated 914 ml hydrogen/g before 5 min and slowly generated approximate 166 ml hydrogen /g in the followed 25 min. Al-3.5wt%Li-20 wt%Ni$_3$Sn$_2$ composite generated 1058 ml hydrogen/g before 5 min and slowly generated 43 ml hydrogen/g in the followed 25 min.

Temperature is a key parameter for the hydrolysis of Al-Li-Ni$_3$Sn$_2$ composites, especially serious effect on the first stage of quick hydrogen generation period. The duration of the quick hydrogen generation period was inversely proportional to hydrolysis temperature while the hydrogen yield was proportional to hydrolysis temperature. The detailed results are shown in Fig.5. Al-3.5 wt%Li-10 wt%Ni$_3$Sn$_2$ composite had approximate 18 min duration and 64% hydrogen yield for the quick hydrogen generation period
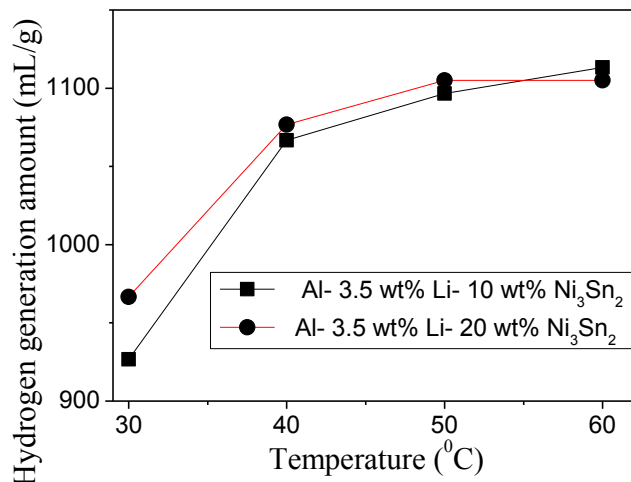
at 30 ^{0}C. It had approximate 10 min duration and 75% hydrogen yield for the quick hydrogen generation period at 40 ^{0}C. The duration continued to be decreased to 5 and 6 min at 50 and 60^{0}C, respectively. The corresponding hydrogen yield increase to 78 and 81% at 50 and 60^{0}C, respectively. Similar phenomenon was also observed for Al-3.5 wt%Li-20 wt%Ni$_3$Sn$_2$ composite. The duration decreased from 6 to 3 min and hydrogen yield increased from 81 to 93% with hydrolysis temperature increasing from 30 to 60^{0}C.The Al-3.5 wt%Li-20 wt%Ni$_3$Sn$_2$ composite had similar hydrogen generation curve at 50 and 60 ^{0}C, reflected that the composite at 50 ^{0}C reached the highest activity.

The apparent activation energy for Al-3.5wt%Li-10wt%Ni$_3$Sn$_2$ and Al-3.5wt%Li-20 wt%Ni$_3$Sn$_2$ composites was calculated to be 39.6 and 28.2 kJ/mol, combined with the Arrhenius equation (1) and the results in Fig.5. The apparent activation energy value less than 40 kJ/mol showed that the hydrolysis reaction of Al-Li-Ni$_3$Sn$_2$ composite was mostly controlled by mass transfer rate. It exhibited that the hydrolysis of Al-Li-Ni$_3$Sn$_2$ composites was an electrochemical process. There was a microgalvanic cell between Al, Li and other metals. Combined with XRD and SEM results, the nanostructure formation of Ni$_3$Sn$_2$, NiSn, AlNi and AlLi distributed on Al surface presented an important role to improve the hydrolysis performance of Al. The effect of Ni$_3$Sn$_2$ was summed up to the following. 1) The formation of fine particles; fine particles was generated with the addition of Ni$_3$Sn$_2$ because Ni$_3$Sn$_2$ was brittle and alloying occurred in the milling process. 2) Nano structure formation of Ni-based alloys deposited on the surface of Al. The structure of Al-(Ni alloy) could act as active sites in the hydrolysis process because AlNi, Al-NiSn and Al- Ni$_3$Sn$_2$ had high electrochemical activity in the hydrolysis process. 3) The increase of Ni$_3$Sn$_2$ concentration in the composite was helpful to decrease the particle size and generate the nanostructure of Al-(Ni alloy). Therefore, the active sites of Al-(Ni alloy) acted as the hydrolysis center and created microgalvanic cells in the water to improve the hydrolysis performance of Al.

Fig.6 shows hydrogen generation amount of Al-Li-Ni$_3$Sn$_2$ com-

posites at different temperature. The composites showed high hydrogen generation amount at 30^{0}C, about 927 and 967 ml hydrogen/g for Al-3.5wt%Li-10 wt%Ni$_3$Sn$_2$ and Al-3.5wt%Li-20 wt%Ni$_3$Sn$_2$, respectively. Their hydrogen generation amount increased to 1067 and 1077 ml hydrogen/g for Al-3.5wt%Li-10 wt%Ni$_3$Sn$_2$ and Al-3.5wt%Li-20 wt%Ni$_3$Sn$_2$ at 40^{0}C, respectively. The Al-3.5wt%Li-20 wt%Ni$_3$Sn$_2$ composite reached theoretic hydrogen generation of 1105 ml hydrogen/g at 50^{0}C. The Al-3.5wt%Li-10 wt%Ni$_3$Sn$_2$ composite continued to increase hydrogen generation amount of 1097 and 1113 ml hydrogen /g at 50 and 60 ^{0}C, respectively.

4. CONCLUSION

The Al-Li-Ni$_3$Sn$_2$ composites were prepared via milling method and their hydrolysis performance was presented in the paper. The milled Al-Li-Ni$_3$Sn$_2$ composites showed high hydrolysis performance at 30-60 ^{0}C, especially that Al-3.5wt%Li-20 wt%Ni$_3$Sn$_2$ had 100% of hydrogen yield and 1103 ml hydrogen/g within 20 min at 50^{0}C. From the results of XRD and SEM, the hydrolysis performance improvement of Al-Li-Ni$_3$Sn$_2$ composite was due to the nano structure formation of Ni-based alloys deposited on the surface of Al. The structure of Al-(Ni alloy) could act as active sites in the hydrolysis process because AlNi, Al-NiSn and Al- Ni$_3$Sn$_2$ had high electrochemical activity in the hydrolysis process. In addition, the alloying of AlNi, Al-NiSn and Al- Ni$_3$Sn$_2$ stimulated the formation of fine particles. Therefore, the addition of Ni$_3$Sn$_2$ which stimulated the fine particles formation on Al surface and created Al-(Ni alloy) active sites was an important factor to improve the hydrolysis performance of Al.

5. ACKNOWLEDGEMENTS

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