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Effects of Cu additives on the hydrogen generation performance of Al-rich alloys

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ABSTRACT

Cu-containing Al-Ga-$InSn_4$ quinary alloys were prepared by a simple smelting method under a high-purity nitrogen atmosphere, and the alloys were cast at room temperature. The microstructures were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) spectroscopy analysis. In addition to the $InSn_4$ intermetallic compounds, elemental Cu was found in the alloys. As the Cu content increased, more holes and cracks were formed, and the Al(Ga) solid solution was pulverized. The melting points of Al compounds with the other elements were determined by differential scanning calorimetry (DSC). The alloy and water reactions were investigated at a water temperature of 40 °C. The Cu addition not only increased the hydrogen yield of the Al-Ga-$InSn_4$ alloys but also stabilized the hydrogen generation from the Al-water reaction, which indicated that the Al-Ga-$InSn_4$-Cu alloys are more suitable as fuel hydrogen sources for proton exchange membrane fuel cells. Based on the DSC and SEM with EDX studies, we propose the reasons for the changes in the Al-water reaction with the Cu addition.

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1. Introduction

Hydrogen is a convenient energy carrier due to its high energy density and environmental friendliness. However, major challenges exist for large-scale applications and a hydrogen-based economy, such as storage safety, convenient hydrogen distribution and release control [1–7]. Since the stored chemical energy of Al can be released by hydrolysis, Al has received attention for on demand hydrogen generation [8–12]. Although Al can react with water, the thin-surface alumina film inhibits a sustained reaction. To remove the alumina film, researchers have adopted various Al-activation techniques, such as Al dissolution in acidic or alkaline solutions [13–16], chemical modification of the Al oxide shell [17], and alloying Al powders with metal additives by milling [18–20]. All these techniques effectively promote the Al-water reaction, but they have some limitations, such as corrosiveness of acidic and alkaline solutions, technical complexity and high -cost of chemical modification, the time cost of milling, and the difficulty of transporting the milled powder. Recently, alloying Al with Ga, In or Sn additives has been developed, which has successfully enabled Al-water reactions. The utilization of bulk alloy ingots, which can be regarded as a type of long-term energy storage, may function well for on-demand preparation of hydrogen.

Water splitting by Al-Ga alloys to produce hydrogen was first reported by Woodall [21,22], but these alloys displayed low reactivity with water at low temperatures. Subsequently, low melting point metals (In, Sn) were added to form bulk Al-rich alloys. Compared with binary alloys, the high-Al Al-Ga-In-Sn alloys can split water continuously even at mild temperatures, and the heat released from the reaction accelerates the generation of hydrogen. Furthermore, the hydrolysis reaction of alloy with high content aluminum can occur and average hydrogen yield will increase after the addition of In and Sn, which improves the efficiency. According to Chen [23,24], an In_3Sn intermetallic compound exists at the grain boundaries at In:Sn weight ratios higher than 15:7, but an $InSn_4$ phase appears with an In_3Sn phase at ratios lower than 15:7. Since Ga and In are expensive and their resources are limited, using $InSn_4$ instead of In_3Sn can significantly reduce costs and avoid the above limitations. However, these two kinds of In and Sn intermetallic compounds have different effects on the hydrogen generation performance of Al-rich alloys [25]. Despite a less efficient hydrogen generation performance than that of the Al-Ga-In_3Sn alloys, the introduction of new components alters the hydrolysis performance

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of Al-Ga-$InSn_4$ alloys.

In the present study, we added Cu to Al-Ga-$InSn_4$ alloys by a traditional smelting and casting method to reduce the contents of Ga and In. Compared with Al-Ga-$InSn_4$, Al-Ga-$InSn_4$-Cu shows an improved hydrogen yield and stable hydrogen generation. The effect of Cu on the hydrogen generation performance of this alloy is comprehensively discussed. Furthermore, the hydrolysis reactions of the Al-Ga-$InSn_4$-Cu alloys were studied at different temperatures, and their kinetic parameters were calculated using an isothermal kinetic model.

2. Experimental

2.1. Synthesis

Alloy ingots with different compositions were prepared (Table 1). The weights of the alloy ingots were controlled at approximately 20 g. In these samples, In and Sn only appeared as $InSn_4$. The copper content was increased from 0 wt% to 5 wt%.

The purity of the materials used in the alloys was 99% for Al and 99.99% for Ga, In, Sn and Cu (particle size: 3–65 μm). The alloys were heated at a rate of 13 °C/min up to 800 °C and maintained at that temperature for 1 h. The entire process was performed under a pure nitrogen atmosphere. Subsequently, the melted alloys were mixed using a propeller for 10 min and removed from the furnace. The liquid metals were then cast into molds and cooled in air. Finally, the alloy ingots were packaged with sealing films and cut to a proper weight and shape for the other experiments.

2.2. Characterization

The alloy ingots were analyzed using a DX-2700 X-ray diffractometer (XRD; Dandong Fangyuan, Dandong, China) with monochromatic Cu Kα radiation ($\lambda_{K\alpha}$ = 1.5406 Å). For the alloy ingots, XRD pattern were collected from 2θ = 30°–80°. After the reactions, the data for the products were scanned from 2θ = 10°–80°. The microstructures and compositions of the alloys were investigated using a HITACHI SU8020 cold field scanning electron microscope (SEM) equipped with a Bruker QUANTAX 200 energy-dispersive X-ray (EDX) spectrometer. To avoid oxidation of the fresh fractural surface, the ingots were placed in the sample chamber immediately after cutting. The reactions between Al and the other intermetallic phases were measured using a PERKIN-ELMER DSC 7 differential scanning calorimeter (DSC). Samples weighing approximately 40 mg were placed in aluminum pans under a high-purity nitrogen atmosphere for the measurements. The heating and cooling cycles were conducted from 25 to 160 °C at a constant rate of 10 °C/min.

2.3. Hydrogen generation measurements

An apparatus similar to the one used in our previous study [25] was used to measure the hydrogen yield. When the distilled water reached a temperature of 40 °C, the alloys were dropped into the water, and the plug was closed immediately. The reaction time was recorded when the hydrogen yield reached 10 ml. During the tests, to maintain the water in the calibrated bottle and gas burette at the same levels, we used a calibrated bottle that could move up and down. A mass flow meter (Alicat Scientific) was used to measure the hydrogen production rate. A drying device was installed between the glass reactor and the mass flow meter. The alloys (0.5 and 1 g) were used in the hydrogen yield and hydrogen generation rate experiments, respectively. During the experiments, the theoretical volumes of hydrogen were calculated from the generation of 1.244 L of hydrogen by 1 g of Al under standard conditions (273 K, 1 atm). The theoretical volumes under the test conditions were then calculated from the ideal gas equation.

All the experiments were repeated at least three times and conducted at room temperature with a humidity below 20%. After the experiments, the precipitates were collected by filtration and dried naturally. The byproducts were also analyzed by XRD.

Table 1
Alloy compositions used for the experiments (wt.%).

Alloy	Al	Ga	In	Sn	Cu
1	80	5	2.92	12.08	0
2	80	5	2.73	11.27	1
3	80	5	2.34	9.66	3
4	80	5	1.95	8.05	5

3. Results and discussion

3.1. Characterization of the alloy ingots

3.1.1. XRD patterns

Fig. 1 shows the XRD patterns of the four samples with different Cu contents. Clearly, the alloys consist of two phases. In and Sn only exist as an $InSn_4$ intermetallic compound (JCPDS file #07-0396). The characteristic peaks of the Al phase (JCPDS file #04-0787) appear, and all the peaks move left slightly at the beginning, showing the existence of an Al(Ga) solid solution [25]. Then, as shown in the enlarged picture in Fig. 1, the peaks of the Al phase began to gradually shift to the right with the increasing Cu content from 0 to 5 wt%. This shift demonstrates the formation of an Al(Cu) solid solution. In contrast to Ga, the atomic radius of Cu is much smaller than that of Al. Clearly, the I(220)/I(111) peak intensity ratio for the low-Cu alloys is larger, indicating that the low-Cu alloys tend to grow with a preferential orientation during solidification, whereas the high-Cu alloys grow homogenously [24]. No significant amount of elemental Cu phase was observed, which may be due to the low Cu content and the dispersion and absence of the formation of a large-area regular structure in the Al alloys.

3.1.2. SEM observations

Fig. 2 shows the SEM images of the Al-Ga-In-Sn-Cu alloys. The fractural surfaces originated from the different amounts of Cu. The Al grains of the alloys have columnar shapes and grow in a definite direction (Fig. 2(a)–(c)). The grain sizes (column widths) of the Al

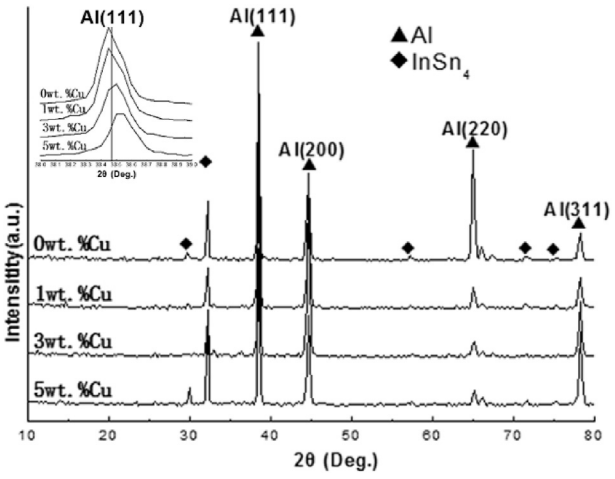

Fig. 1. XRD patterns of the remnant alloys. The inset (enlarged plot) shows the slight change in the Al (111) peak position.

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