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Reactivity of Al-rich Alloys with Water Promoted by Liquid Al Grain Boundary Phases

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Al–Ga–Sn, Al–Ga–In and Al–Ga–In–Sn alloys were prepared using arc melting technique. Their microstructures were investigated by X-ray diffraction and scanning electron microscopy with energy dispersed X-ray. Based on microstructure analysis, the phase constituents of alloys at Al grain boundaries were identified. The melting points of Al grain boundary phases were measured using differential scanning calorimeter. The reactivities of Al–water at different water temperatures indicate that liquid Al grain boundary phases promote Al–water reactions of alloys. The melting points of Al grain boundary phases affect the reaction temperatures of Al–water, leading to different reaction temperatures of alloys. The measured H_2 generation rate and yields of alloys are related to the compositions of alloys. The theory of micro-galvanic cell is used to explain the observed different H_2 generation rates of alloys.

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1. Introduction

Al as a high-capacity energy storage material has received much attention for H_2 producing applications[1–8]. Pure Al, however, is not capable of producing H_2 from water because a thin oxide film on Al surfaces prohibits Al to react with water[9–14]. Alloying Al with low melting point metals (Ga, In, Sn) was suggested a feasible way of producing H_2 from water[15–18], for those metals may disrupt Al oxide film formed on Al. Bulk alloys containing low melting point metals can split water at a mild temperature[19–21], exhibiting a huge potential of H_2 producing applications if those low melting point metals are fully recycled.

The mechanism of Al splitting water was ascribed to the low melting point phases formed in alloys, through which Al atoms of Al grains are able to diffuse and reach reaction sites to split water. Previous results[22,23] found that the reaction temperature of Al with water is closely related to the melting point of Al grain boundary (GB) phases in alloys. For example, in the Al–Ga–In–Sn quaternary system, the alloys displayed reactivity at a temperature above the freezing point of water, lower than the Ga–In–Sn eutectic melting point of 10.7 °C[24]. Al–Ga binary alloys are observed to produce H_2 at a reaction temperature of about 26 °C[19], very close to the melting point of Al–Ga eutectic[25]. These results suggested that the higher the melting point of the reaction-enabling phases, the higher the reaction temperature of Al–water. In other words, the reaction temperature of Al–water can be adjusted by modifying the melting point of the low melting point phases in alloys. It is no doubt that this is important for the application of alloys if their reaction temperatures are controllable. According to phase diagrams[26,27], the melting points of Ga–In and Ga–Sn binary eutectics are 15.3 °C and 20.5 °C, respectively. These binary eutectics can act as reaction-enabling phases to initiate the reactivity of Al alloys with water. So far, research work on the reactivity of Al–Ga–In and Al–Ga–Sn alloys with water is scarce. Whether these alloys will react with water at a low or a high reaction temperature is unknown.

In this paper, Al–Ga–Sn, Al–Ga–In and Al–Ga–In–Sn alloys were prepared, and their reactivity with water was performed at different temperatures. The reaction temperatures of alloys were investigated and compared with the melting points of Ga–In and Ga–Sn binary eutectics together with the previously reported results. The mechanism of reactivity of alloys with water was discussed.

2. Experimental Details

Al–Ga–Sn, Al–Ga–In, and Al–Ga–In–Sn alloy ingots with different compositions were prepared by using arc melting technique. The mass ratio of Ga/Sn and Ga/In is 1.73:1 for Al–Ga–Sn and Al–Ga–In alloys, and the mass ratio of Ga/In/Sn is 3.8:1.5:0.7 for Al–Ga–In–Sn alloy. Those ingots were melted under high purity argon

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atmosphere in a water-cooled copper crucible for several times to ensure a homogeneous composition.

The phase compositions of alloys were identified by X-ray diffraction (XRD) using a Rigaku D/max 2400 diffractometer with monochromated CuK_α radiation ($\lambda_{k\alpha 1}$ = 0.154056 nm). The fracture morphologies of alloys were characterized by using an FEI Inspect F50 scanning electron microscope (SEM) with a Quanta 600 EDX (Energy Dispersed X-ray) system. In order to minimize the oxidation of the fresh fracture surface, all samples were placed into the sample chamber as soon as they were broken. The equilibrium solubility of Ga in Al at room temperature is about 15 wt%, but In and Sn are nearly immiscible in Al. Hence, part of Ga and most In and Sn will precipitate at Al grain boundaries after the solidification of alloys, leading to brittleness of the prepared alloys. Since the alloys are fractured in an intergranular manner, Al grains and grain boundary phases are observed directly using SEM.

A differential scanning calorimeter (DSC) Q1000 made by TA Instruments (New Castle, DE) was used to measure the melting points of Al grain boundary phases. The instrument was calibrated by testing the melting point of a reference material (In). Samples of about 40 mg were run using Al pans under flowing purified argon. One heating and cooling cycle was conducted on samples in a temperature range from –30 to 300 °C with a constant heating and cooling rate of 10 °C/min.

The equipment used in H_2 generation experiments is shown in previous works[22,23]. A 250-mL Pyrex glass reactor containing 200 mL of distilled water was placed in a water bath to maintain a constant temperature. After the reactor reached the targeted temperature, the sample placed on a tray above the water level was dropped into the water. The weight of ejected water due to H_2 release was recorded automatically using a one ten-thousandth scale, and then these data and reaction time were stored in a computer. The water mass was converted to H_2 generated volume under the standard conditions (273 K, 1 atm) using the ideal gas equation. The reactions of Al–water were conducted at different water temperatures. For each experiment, the mass added into the reactor was about 0.3 g, and the testing was repeated at least three times. The averaged H_2 generation rates were also calculated for each comparison of reaction rate of different samples. In this calculation, the data of H_2 yield below 50% of H_2 production curve was selected to extract the H_2 generation rate of a sample. Its value was obtained by calculating the slope of the selected curve using linear curve fitting. The results given here represent the averages for three repeated measurements.

3. Results and Discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of Al–Ga–Sn and Al–Ga–In alloys. All samples contain crystalline Al. Besides Al, In and Sn phases are found in Al–Ga–In and Al–Ga–Sn alloys, respectively. Similar to previous observation[22,23], intermetallic compound In_3Sn (β) phases are found in Al–Ga–In–Sn alloy (not given).

3.2. SEM and EDX observations

Fig. 2 shows SEM images of fracture surface of Al–Ga–Sn and Al–Ga–In alloys. Al grains are columnar showing obvious directional growth of Al grains during solidification of alloys. Their grain sizes (column width) range from 30 to 60 μm. EDX analysis (Tables 1 and 2) shows that Al grains mainly contain Al and little Ga. Al grain surfaces are covered with lots of dispersed white or gray phases, whose shape and size depend strongly on the composition of alloys.

As shown in Fig. 2(a) and (b), when contents of low melting point (l.m.p) metals in Al–Ga–Sn alloys are below 10 wt%, the GB phases

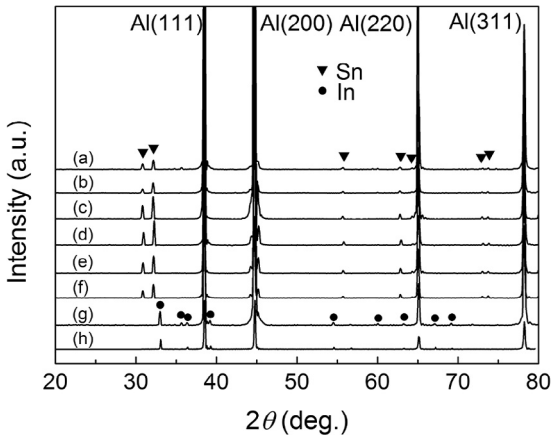

Fig. 1. XRD patterns of Al–Ga–Sn and Al–Ga–In alloys: (a) 3 wt% Al–Ga–Sn, (b) 6 wt% Al–Ga–Sn, (c) 8 wt% Al–Ga–Sn, (d) 10 wt% Al–Ga–Sn, (e) 12 wt% Al–Ga–Sn, (f) 15 wt% Al–Ga–Sn, (g) 15 wt% Al–Ga–In, (h) 3 wt% Al–Ga–In.

are granular and rode-like, and their sizes increase with rising the contents of l.m.p metals in alloys. The EDX analysis shows that the phases contain lots of Sn, little Ga and Al. The atomic ratio of Al:Sn in most phases is close to the Al:Sn atomic ratio of 2.1:97.9 of Al–Sn binary eutectics under equilibrium solidification[28]. Therefore, those GB phases are identified as Al–Sn binary eutectics. When contents of l.m.p metals in alloys are higher (>10 wt%), the sizes of GB phases become bigger and the compositions are inhomogeneous. Besides little amount of isolated Al–Sn binary eutectics particles, many GB phases are presented with bigger plates, which are mixtures containing Al–Sn binary eutectics and Ga-rich phases. As indicated in Fig. 2(d), in contrast to the bright white Al–Sn eutectics, the Ga-rich phases are dark gray, and Al and Ga rich, but lack of Sn. The Ga:Sn atomic ratios of those Ga-rich phases are scattered as detected by EDX. The measured Ga:Sn atomic ratios range from about 4:1 to 11:1, indicating that some phases are Al–Ga–Sn eutectics as their atomic ratios approach 88.9:7.9 of Al–Ga–Sn ternary eutectics under equilibrium solidification[29,30]. But the Ga:Sn atomic ratios of others deviate markedly from 88.9:7.9, suggesting that those phases also contain extra Sn besides Al–Ga–Sn eutectics.

From Fig. 2(e)-(h), one can see that the Al–Ga–In alloys exhibit similar features of metallographic morphologies as those of Al–Ga–Sn alloys because of similar solidification process of two kinds of alloys. In Al–Ga–In alloys, Al–In binary and Al–Ga–;In ternary eutectics are identified as pointed by arrows.

According to the liquidus projection of ternary phase diagram of Al–Ga–Sn alloys (Fig. 3), the mass percentages of structural components are calculated by means of lever rule (Table 3). It can be seen that the amount of Al–Sn binary eutectics increases with increasing Ga and Sn content as their content in alloys is below 10 wt%. However, their amounts reduce due to the presence of Al–Ga–Sn ternary eutectics when Ga and Sn content is above 10 wt%. With further increasing the content of Ga and Sn, the amount of Al–Ga–Sn eutectic increases. The results indicate that both the type and mass percentage of phase components at Al grain boundaries are closely related to the content of l.m.p metals added in alloys, for these metals will form different phases at Al grain boundaries during solidification. Due to lack of liquidus projection of ternary phase diagram of Al–Ga–In alloys, the mass percentages of structural components of the alloys are not extracted.

3.3. DSC findings

Fig. 4 shows the DSC curves of Al–Ga–Sn and Al–Ga–In alloys tested at the heating cycle. As the content of l.m.p metals of Ga and

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