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Effects of Bi composition on microstructure and Al-water reactivity of Al-rich alloys with low-In

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ABSTRACT

Bi-bearing Al-Ga-In-Sn quinary alloys were prepared by a high-temperature melting technique. The alloys primarily consist of Al(Ga) matrix and Ga, In, Sn, Bi (GISB) grain boundary phase, mainly in the form of Ga-$InSn_4$-InBi. The microstructure of GISB particles was obviously equiaxed with the increasing Bi dosage. Al-water reaction was tested at 40 °C. Owing to the Bi-doping, the hydrogen generation yields of alloys with $InSn_4$ intermetallic compound are obviously improved and hydrogen release rates gradually tend to be stable, which show great potential in applications. At the dosage of 2.53 wt% Bi, the hydrogen generation performance of alloys was more prominent in Al-water reaction, including a theoretical hydrogen generation yield and hydrogen released extremum rate to ~0.076 L/min·g Al alloy. Furthermore, the Al-water reaction mechanism of Bi-bearing Al-rich low-In quinary alloys has been put forward.

Introduction

The environmental pollution and fossil storage decline is transforming the current energy-resource structure from traditional energy to clean energy [1,2]. Hydrogen is recognized as the greatest potential energy of the 21st century because of its ideal high calorific value, highest gravimetric energy density and non-polluting combustion products [3,4], which are greatly beneficial to various hydrogen energy applications. The common methods for industrial hydrogen preparation, include water electrolysis [5–8], methanol reforming [9] and fossil fuels reforming [10]. Recently, the Al hydrolysis method has drawn much attention for hydrogen generation, especially for the on-demand hydrogen supply system [10–13]. This method solves some application problems, such as the storage and transportation limitations of hydrogen [14–17]. However, pure Al cannot react with water at room temperature or even higher because the thin oxidation film (alumina) adheres to the Al surface. Besides the general activated methods, such as chemical modification of the alumina film [18] and mechanical milling by employing different additives [19–21]. Al can be activated by alloying with low-melting-point metals (e.g. Ga, In, Sn) [22–26], which only act as a reaction medium, rather than being consumed in the Al-water reaction. These Al-alloy bulks not only benefit

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the storage and transportation during process, but also reduce the preparation cost by recycling low-melting-point metals, which show a bright prospect for application of hydrogen.

Generally, a small amount of low-melting-point metals are contained in the Al matrix, but the majority exist in the grain boundary (GB) phase, mainly in the form of single substances or intermetallic compounds, such as In_3Sn or $InSn_4$. As reported, the quantity and size of GB-phase particles are closely related to Al-water reactivity of Al-rich alloys [27–29]. The relationship between hydrogen released rate and the microstructure of GB-phase particles can be clarified by an analytical expression [27]. However, the changing compositions how to influence the microstructure of GB-phase has been rarely investigated. It is noteworthy that Ga-In-Sn eutectic in GB-phase primarily in the form of Ga-In_3Sn, which has the lowest melting point around 10.4 °C [30]. This is the reason why Al-water reaction could initiate at a considerable lower temperature. Correspondingly, the hydrogen production performance of alloys can be significantly improved. Since the price of indium is high, the addition of more indium increases the cost of preparation. Unfortunately, the alloys with $InSn_4$ intermetallic compound, which is greatly cheaper than In_3Sn, present poor hydrogen generation performance during Al-water reaction. So far, there is no deep study about how to improve hydrogen generation performance of Al alloys containing $InSn_4$ intermetallic compound.

Herein, Al-Ga-In-Sn-Bi alloys containing $InSn_4$ intermetallic compound were prepared. The growth of GB-phase particles was investigated by adjusting the composition in alloys. Besides, the influence mechanism of GB phase on hydrogen generation performance was further clarified via hydrogen generation test. An optimal component of Al alloy with great potential in application was presented, which shows a steady rate of hydrogen production under the premise of full energy conversion.

Experimental

Al-Ga-In-Sn-Bi alloys (20 g) were prepared by a high-temperature melting technique, with the Bi content increasing from 1.41 to 3.01 wt%. The low-melting-point components were maintained at 10% with a constant 2.5 wt % Ga (Table 1). All raw materials used were purities over 99%. The alloys were melted at 800 °C with a heating rate of 10 °C/min and kept at this temperature for 1 h. The entire fabrication process was conducted under high-purity flowing nitrogen atmosphere before casting. Then, molten alloys were taken out of the furnace, casted and kept in vacuum until they naturally cooled to room temperature.

Table 1 – Compositions of quinary Al-alloy ingots (wt.%).

Alloy	Al	Ga	In	Sn	Bi
Bi-free	90	2.5	1.46	6.04	0
1	90	2.5	1.81	4.28	1.41
2	90	2.5	1.88	3.90	1.72
3	90	2.5	2.00	3.31	2.19
4	90	2.5	2.09	2.88	2.53
5	90	2.5	2.21	2.28	3.01

The phase compositions of the quinary alloys were analysed using a DX-2700 X-ray diffractometer (XRD, Dandong Fangyuan, China) from 10 to 80° and with monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å). The alloy microstructures were characterized by a scanning electron microscope (SEM) with a Bruker QUANTAX 200 energy dispersed X-ray (EDX) system. Each sample after breakage was immediately placed into the sample chamber to minimize the interference of oxidation on fresh fracture surfaces. Both melting and solidification behaviours of alloys were analysed by PERKIN-ELMER DSC 7 differential scanning calorimetry (DSC), in which heating and cooling cycles were tested at a constant rate of 5 °C/min, with temperature rising from −20 to 200 °C. The equipment used in the hydrogen generation performance test including a hydrogen generation device and a quantization system was reported in our previous work [31]. A glass reactor containing 100 ml of distilled water was placed in a water bath to stabilize the temperature. All experiments were conducted in the same conditions, including room temperature at 10 °C and humidity below 20%. Once the water temperature reached 40 °C, a 0.5 g sample was dropped into the glass reactor. While the lifting platform was adjusted immediately to keep the calibrated bottle and gas burette at the same water level. The hydrogen yield, equal to the weight of the ejected water, was recorded at once. The theoretical hydrogen yield under test conditions was calculated using the ideal gas equation that 1.244 L of hydrogen with 1 g of Al under the standard conditions of 273 K and 1 atm. The hydrogen generation rate of about 1 g ingot was monitored by a flowmeter (Alicat Scientific) with the accuracy of part per thousand. The corresponding data stored in a computer at interval of 0.1 s was employed to compare the duration time and average hydrogen generation rate between different quinary Al-alloys.

Results

Characterization of Al-Ga-In-Sn-Bi quinary alloys

XRD analysis

Fig. 1 displays the XRD patterns of Al-Ga-In-Sn-Bi alloys. Clearly, all alloys contain Al(Ga) solid solution (PDF 04#0787) and intermetallic compound $InSn_4$ (PDF 48#1547), but the InBi

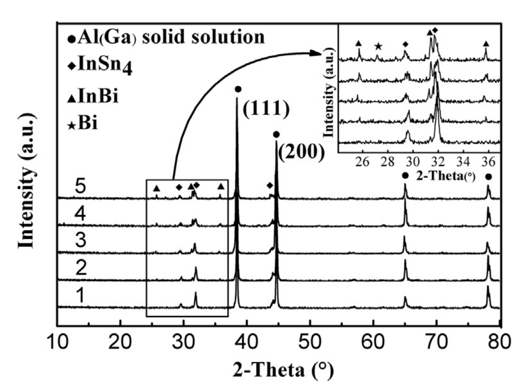

Fig. 1 – Typical XRD patterns of quinary Al-Ga-In-Sn-Bi alloys and partial amplification.