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Grain refinement and Al-water reactivity of Al–Ga–In–Sn alloys

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ABSTRACT

Al–Ga–In–Sn alloys were prepared by using traditional casting metallurgy method with different additions of Al–5Ti–1B grain refiner. Their microstructures were investigated by means of X-ray diffraction (XRD) and scanning electron microscope (SEM) with energy dispersed X-ray (EDX). The Al grains of alloys are refined significantly from 129 μm to 57 μm with increasing Ti content from 0.03 wt% to 0.24 wt%. Many thin dendrites that are a few micrometers thick are observed within Al grains.

Al-water reactivities were performed under different water temperatures. The alloy with Ti content of 0.12 wt% shows the maximum H_2 generation rate under different water temperatures, which is above 5 times of Ti-free alloy. The H_2 yields of alloys drop from 87% to 30% with rising Ti content from 0.03 wt% to 0.24 wt% at the water temperature of 30 °C, but they rise to about 90% when the water temperature is above 50 °C.

The growth mechanism of alloys and the effect of grain refinement on Al-water reactivities are discussed.

Introduction

Producing hydrogen using Al to split water has attracted much attention since Al is light weight and abundant in nature [1–20]. In addition, the resultant by-products of Al-water reaction are environment friendly and can be fully recycled [21,22].

Pure Al will not split water because a dense layered oxide film on Al surface prohibits Al to react with water [23]. Alloying Al with low melting point metals (Ga, In, Sn) was a feasible way of producing H_2 from water, for those metals can disrupt Al oxide film formed on Al [24–33]. The reactivity of the alloy with water has been investigated in detail. 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 [32,33].

The advantages of the method include: low temperature reaction with water, easy storage, and high hydrogen yield, exhibiting a huge potential of H_2 producing application of the alloy. However, this method also suffers from disadvantages. Ga and In are expensive and difficult to be extracted from by-products. In addition, the H_2 generation rate of the bulk Al alloys is only 1/50 of that of Al powders activated by ball milling [34,35], indicating a relatively lower H_2 generation rate of the alloy prepared using this method.

Previous results found that the Al grain size, the size and number of Ga–In–Sn (GIS) phase were key factors to control

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the hydrogen generation rate of Al-water reaction [32,35–37]. Further studies show that the H_2 generation rate of Al-water reaction is connected with the area of β (In_3Sn) phase covering on Al [37]. Since the β area increases with Al grain refinement, the alloy displays higher hydrogen generation rate as Al grains are refined.

In fact, making an alloy with finer Al grains is desirable since Al reacts fast with water and there will be high H_2 yields because more Al has been converted into hydroxides [32]. However, it is difficult to prepare bulk ingot with finer Al grains just by means of increasing cooling rate of Al solidification [32].

Adding grain refiner is an effective way of grain refinement. Ti is often used to refine Al alloys [38–41]. According to Al–Ti binary phase diagram, $TiAl_3$ can be formed in Al melt, when Ti content is above 0.15 wt%. At the temperature of 665 °C, peritectic reaction: $Liquid + TiAl_3 \rightarrow \alpha\text{-}Al$ will take place in liquid, accelerating nucleation of Al grain.

If pure Ti as a grain refiner is added in alloy, its efficiency on Al grain refinement is not ideal. Experiments show that when 0.5 wt% Ti is added in alloy, all the Al grains are transformed into equiaxed with an averaged size of about 100 μm [36]. Although Al grains are refined, the H_2 generation rate of the Ti-bearing alloy is not increased compared with that of Ti-free alloy, meanwhile the H_2 yield of Ti-bearing alloy is also reduced significantly [36]. Ti with such a high content in alloy will occupy some sites for Al contacting with water and form a thin inert Ti layer on Al, resulting in Al-water reaction was prohibited [36].

Al–Ti–B is reported to be a good grain refiner of Al alloy since Al–Ti–B favors $TiAl_3$ particle formation in Al melt [42–45]. $TiAl_3$ is effective nucleation site for Al grain to nucleate due to its coherent relationship with α-Al, but $TiAl_3$ is unstable in Al melt due to its low melting point. However, TiB_2 has high melting point of 3225 ± 25 °C [46], it exists in Al melt stably. Some free Ti atoms will segregate on TiB_2 surface to form $TiAl_3$ with Al during continuous concentration fluctuation of Ti atoms in Al melt [47–49]. Therefore, element B increases the nucleation sites for Al to nucleate, so that Al grains are refined effectively. Thus, it is reasonable that less Al–Ti–B is required to refine Al alloy compared with pure Ti grain refiner.

So far, what amount of Al–Ti–B will refine the Al–Ga–In–Sn alloy effectively is unknown. How the grain refinement affects the hydrogen generation performance of Al alloy is also not clear.

In the present paper, Al–Ga–In–Sn alloys containing different contents of Al–5Ti–1B were prepared by using traditional casting metallurgy method. The microstructures of alloys were detected using XRD, SEM and EDX. The reactivity of alloys with water at different temperatures was investigated. The growth mechanism and the hydrogen generation performance of alloys were discussed.

Experiments

Eight Al alloy ingots in 200 g quantities were made by using traditional casting metallurgy method with different additions of Al–5Ti–1B. The compositions of low point metals were controlled to Al-3.8 wt% Ga-1.5 wt% In-0.7 wt% Sn for each ingot. The nominal compositions of alloys are listed in Table 1. Purities over 99.99% of Al, Ga, In, Sn and commercial Al–5Ti–1B wire are used as starting materials.

The ingots were melted with a graphite crucible at 750 °C in a closed electric furnace. Then, the melt was hold in crucible at this temperature for 10 min after the addition of the desired amount of grain refiner. In order to ensure a homogeneous composition of alloy, the melt was stirred with a clay-bonded steel ladle for about 30 s, then cast into a prior heated steel mold of 150 °C.

Alloy ingots were cut into 1 cm square and 2 mm thick pieces, which were used to do microstructure analysis and reactivity measurement of Al-water. The phase compositions of alloys and reaction products were analyzed by X-ray diffraction (XRD) using a Rigaku D/max 2400 diffractometer with monochromated CuKα radiation ($\lambda_{k\alpha} = 0.154056$ nm).

The microstructures of alloys and by-products were characterized using FEI inspect F50 scanning electron microscope (SEM) with a Quanta 600EDX (Energy Dispersed X-ray) system. In order to minimize the oxidation of the fresh fracture surface, the samples were placed into the sample chamber as soon as they were broken.

The equipment used in H_2 generation experiments had been described in previous study [35]. The reaction temperatures of Al-water were conducted at 30 °C, 50 °C and 70 °C, respectively. 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 calculated for different alloys. In those calculations, the data of H_2 yield below 80% on H_2 production curves were selected to extract the H_2 generation rates of samples by calculating the slopes of the selected curves using linear curve fitting. The results given here represent the averages for three repeated measurements. The room of experiments was controlled at a constant temperature of 20 °C and humidity below 20%.

Results

Microstructure of Al alloys

XRD analysis

Fig. 1 shows the XRD patterns of Al alloys with different Ti contents. All Al alloys consist of Al (Ga) solid solution and intermetallic In_3Sn, similar to the previous observations [32]. It can be seen that the Al peak intensity ratio of $I_{(111)}$ to $I_{(200)}$ of Ti free Al alloy is about 0.27, weaker than that of 2.128 (PDF

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

Alloy code	Ti	Ga	In	Sn	Al
1#	0	3.8	1.5	0.7	Bal.
2#	0.03	3.8	1.5	0.7	Bal.
3#	0.06	3.8	1.5	0.7	Bal.
4#	0.09	3.8	1.5	0.7	Bal.
5#	0.12	3.8	1.5	0.7	Bal.
6#	0.15	3.8	1.5	0.7	Bal.
7#	0.18	3.8	1.5	0.7	Bal.
8#	0.24	3.8	1.5	0.7	Bal.

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