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

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[Received 10 June 2015; Received in revised form 18 August 2015; Accepted 19 August 2015]

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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 microscope 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 H₂ 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 H₂ generation rates of alloys.

Key words: Al alloy; Microstructure; Composition; Reaction; Hydrogen generation rate

1. Introduction

Al as a high-capacity energy storage material has received much attention for H₂ producing applications^[1-8]. Pure Al, however, is not capable of producing H₂ 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 H₂ 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 H₂ 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 H₂ 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. 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 atmosphere in a water-cooled copper crucible for several times to ensure a homogenous 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 ($\lambda_{\text{CuK}\alpha 1}$ =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 H₂ generation experiments is shown in previous work^[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 H₂ 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 H₂ 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 H₂ generation rates were also calculated for each comparison of reaction rate of different samples. In this calculation, the data of H₂ yield below 50% of H₂ production curve was selected to extract the H₂ generation rate of a sample. Its value was obtained by calculation 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 In₃Sn (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 grey 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 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 grey, 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 mean 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 amount reduces 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 Sn in Al-Ga-Sn alloys is below 10 wt%, only one endothermal peak is seen in DSC traces with a peak temperature of about 218 °C, which is close to the melting point of Al-Sn binary eutectic of 228 °C^[28]. When the content of Ga and Sn is above 10 wt%, besides the peak at 218 °C, a sharp endothermal peak of about 18.9 °C is detected, which is very close to the melting point of Al-Ga-Sn ternary eutectic of 19 °C^[29]. This peak displays higher intensity with the increase of the content of Ga and Sn in alloys, implying that the higher the content of Ga and Sn, the more the Al-Ga-Sn ternary eutectics in Al-Ga-Sn alloys. Additionally, a wide endothermal peak is observed with a peak temperature of about 120 °C in DSC curve of 15 wt% Al-Ga-Sn. This peak may be caused by more extra Ga dissolving in Al-Sn eutectics and giving rise to an extended melting range of the Ga and Al-Sn eutectic mixtures upon liquefaction.

Similar to Al-Ga-Sn alloys, a small endothermal peak at about 152 °C is shown in Al-Ga-In alloys, as a result of melting of Al-In binary eutectic, whose melting point is 156 °C^[31]. The 15 wt% Al-Ga-In alloy also displays a sharp peak at 15 °C and a diffusive peak at 82 °C, which corresponds to the melting of Al-Ga-In ternary eutectics, and Ga and Al-Sn eutectic mixtures, respectively. From Fig. 4, the melting points of eutectics of Al-Ga-Sn and Al-Ga-In alloys are extracted to be 18.9 °C and 15 °C, respectively, higher than the measured melting point of Al-Ga-In-Sn eutectic (10.7 °C^[24]).

3.4. Performance of H₂ generation

The reactivity of the Al-Ga-Sn and Al-Ga-In alloys with water was tested at different water temperatures using the H₂ measurement apparatus, and their reaction temperatures are roughly estimated. Fig. 5 shows H₂ production curves of Al-Ga-Sn alloys at different water temperatures. When the Ga and Sn content in alloys is below 10 wt%, the alloys did not show reactivity within the temperature range of from 10 to 70 °C. The alloys with high content of Ga

and Sn (> 10 wt%), however, are observed to produce H_2 at different reaction temperatures, even though their H_2 yields are very low. For example, the 15 wt% alloy reacts with water at about $20\text{ }^{\circ}\text{C}$, but 12 wt% and 10 wt% alloys at about $30\text{ }^{\circ}\text{C}$. The H_2 yield of 15 wt% alloy is 12%, and the H_2 yields of 10 wt% and 12 wt% alloys are below 10%. The remains of reaction were observed using SEM to look for the reasons that Al is not depleted. From the SEM, it is noted that Al surfaces of remains contain lots of oxygen, and their color turns from silver white into dark grey.

From Fig. 5, one can see that the H_2 yields show an increasing trend with increasing water temperature. At a water temperature of $70\text{ }^{\circ}\text{C}$, the H_2 yields of 10 wt%, 12 wt% and 15 wt% alloy are 25%, 70% and 90%, respectively, indicating the big difference of H_2 yields of those alloys. From Fig. 5, the H_2 generation rates of alloys are calculated, and their relations with Ga and Sn content at different water temperatures are plotted in Fig. 6. At the same water temperature, the H_2 generation rates of alloys increase with increasing Ga and Sn content when Ga and Sn content is higher than 10 wt%.

Fig. 7 shows H_2 production curves of Al-Ga-In alloys at different water temperatures. Different from the reactivity of Al-Ga-Sn alloys, the Al-Ga-In alloys displayed reactivity at about $10\text{ }^{\circ}\text{C}$. The H_2 yields are above 90% for 3 wt% alloy at $50\text{ }^{\circ}\text{C}$ and 15 wt% alloy at $20\text{ }^{\circ}\text{C}$, indicating the nearly complete consumption of Al in those alloys. Fig. 8 shows the calculated H_2 generation rates of Al-Ga-In alloys at different water temperatures. The calculated results of 15 wt% Al-Ga-Sn alloy and 15 wt% Al-Ga-In-Sn alloy are also plotted in this figure. As shown in Fig. 8, the H_2 generation rates of 15 wt% Al-Ga-In alloys are higher than those of 3 wt% alloys. With increasing water temperatures, the H_2 generation rates of 3 wt% Al-Ga-In alloy increase slightly, but the H_2 generation rates of 15 wt% Al-Ga-In alloy increase significantly. When water temperatures are below $30\text{ }^{\circ}\text{C}$, the H_2 generation rates of 15 wt% Al-Ga-In and Al-Ga-Sn alloys are lower than those of 15 wt% Al-Ga-In-Sn alloy. However, when water temperatures are above $30\text{ }^{\circ}\text{C}$, the 15 wt% Al-Ga-In alloy exhibits the lowest H_2 generation rate, but the 15 wt% Al-Ga-Sn alloy exhibits the highest one. For example, at a water temperature of $70\text{ }^{\circ}\text{C}$, the H_2 generation rate of 15 wt% Al-Ga-In, Al-Ga-In-Sn and Al-Ga-Sn alloys are 583, 1256, 1595 ml/min g Al, respectively.

3.5. Discussion

Present and previous experiments confirmed that the observed Al splitting water reaction is promoted by liquid GB phases, such as: Al-Ga-In-Sn, Al-Ga-Sn, Al-Ga-In and Al-Ga

eutectics, since those GB phases on Al not only protect Al from oxidation but also provide a pathway for Al diffusion to the reaction site as well. Considering the reaction of an Al grain with part of surface covered with GB phases in water, Al embedded in GB phases react with water firstly because the GB phases contain a certain amount of Al. The reaction depletes the equilibrium concentrations of Al in GB phases. Clearly, if the GB phases are solid, Al atoms of Al grain is not likely to enter into the GB phases to compensate the Al consumed by reaction with water in GB phases. Once Al in the GB phases contacting water is all consumed, Al-water reaction suspends. For this reason, it is often observed that a slight of bubbles emit from the sample surface for about tens of seconds, and then disappear, indicating that Al-water reaction is not really initiated. However, when the GB phases are liquid (the water temperature is higher than the melting point of GB phases), Al embedded in GB phases diffuses freely in the liquid. As a result, Al atoms of Al grain covered by GB phases will enter into the liquid to restore the Al concentration of liquid. This was confirmed by the SEM observation that a large number of Al nanoparticles (about 50–100 nm in diameter) were embedded in the Ga-In-Sn eutectic phase^[20]. During the reaction, the resulting hydroxide precipitates will be swept away by H₂ bubbles and escape from the surfaces of GB phases. Meanwhile, the surfaces of GB phases move inwards due to mass lose of Al on the covering area of GB phases. As Al continues to diffuse into GB phases, Al reacts with water continuously until all of Al in alloy is consumed.

Clearly, the mechanism of Al-water reaction works based on the presence of liquid phases at Al grain GBs. When Ga and Sn content in Al-Ga-Sn alloys is below 10 wt%, the alloys just contain Al-Sn binary eutectic (which melting point is 218 °C), whereas Al-Ga-Sn ternary eutectics are absent. As a result, the Al-Ga-Sn alloys are unable to split water. However, when Ga and Sn content in Al-Ga-Sn alloys reaches 10 wt%, due to the presence of Al-Ga-Sn ternary eutectics with a melting point of 18.9 °C in alloys, Al is capable of reacting with water.

The mechanism of Al-water reaction predicts that there exists a critical reaction temperature related to the melting point of GB phases for each alloy. When water temperature is below the reaction temperature of an alloy, Al is inert in water. Once water temperature approaches or is up to the reaction temperature of an alloy, Al begins to react with water. Therefore, it is reasonable that the alloys exhibit different reaction temperatures, because of different melting points of those GB phases in alloys. As observed from experiments, Al-Ga-In-Sn and Al-Ga-In alloys are capable of splitting water at about 1 °C^[22,23] and 10 °C, respectively. Their reaction temperatures are smaller than their melting points of GB phases. However, the reaction temperatures of 15 wt% Al-Ga-Sn and 50 wt% Al-50 wt% Ga alloys are about 20 °C and 26 °C^[19], respectively, close to their melting points of GB phases. The results

indicate that the alloys react with water at higher temperatures as their melting points of GB phases are higher, for the melting point of GB phases follows sequence of $T_{AG} > T_{GS} > T_{GI} > T_{GIS}$ (A, G, I, S refer to Al, Ga, In, Sn, respectively), consistent with the temperature sequence of Al-water reaction of alloys. It is noted that the reaction temperatures of some alloys, such as: Al-Ga-In and Al-Ga-In-Sn alloys display a few degree Celsius lower compared with their melting points of GB phases. The results seem to conflict with the reaction mechanism mentioned above, as the GB phases are solid in alloys at those lower water temperatures. In fact, Al solvated in GB phases can react with water. Since the reaction releases a large amount of heat, the temperature is increased at the local reacting region. If the releasing heat induces GB phases transform from solid to liquid, Al will react with water continuously.

Compared with 15 wt% Al-Ga-Sn alloy, the 10 wt% and 12 wt% Al-Ga-Sn alloys exhibit a higher reaction temperature of about 30 °C, although they contain Al-Ga-Sn eutectic with the same a melting point of 20 °C as 15 wt% Al-Ga-Sn alloy (Fig. 4). The result is inconsistent with the theory that Al reacts with water at a temperature approaching the melting point of GB phase. Since the later two alloys consist of less Al-Ga-Sn eutectic than the former one (Fig. 4), the less GB phase is ascribed to the observed higher reaction temperature of 10 wt% and 12 wt% Al-Ga-Sn alloys. In fact, when Al reacts with water, Al grain surface is passivated continuously during the reaction. If gas flow of H₂ bubbles is intense enough as a result of vigorous reaction of Al-water, the passivated hydroxide film on Al will be swept away so that the fresh Al surface is exposed, sustaining the reaction until most Al is depleted. Conversely, an Al hydroxide layer will be formed on the fresh Al surface. The reaction will retard or stop if the adhesive hydroxide layer on Al attains a critical value. As the 10 wt% and 12 wt% Al-Ga-Sn alloys contain less GB phase, it is likely that the generated H₂ bubbles of reaction are unable to disrupt the hydroxide film formed on Al. Thus, it is reasonable that they are not capable of splitting water at 20 °C. When the water temperature rises up to 30 °C, the amount of Al-Ga-Sn eutectic will increase due to the reaction of original Al-Ga-Sn eutectic in alloys with neighboring Al-Sn eutectic. In addition, Al also reacts with water quickly at a higher temperature. These factors result in Al to split water continuously.

Although the above theory can explain well the reaction temperatures of alloys, but it is difficult to explain the observed reaction rates and yields of alloys. Results show that when the water temperature is above 30 °C, the H₂ generation rate of 15 wt% Al-Ga-In-Sn alloy is not highest anymore. Instead, the 15 wt% Al-Ga-Sn alloy exhibits the highest H₂ generation rate, while the 15 wt% Al-Ga-In alloy exhibits the lowest one. The result suggests that Al-water reaction speed of alloys is not determined by the melting point, but by the compositions of

eutectic GB phases. The theory of micro-galvanic cell^[32-36], which is often used to explain Al corrosion in many Al alloys, can be used to interpret the observed phenomenon of reactions. In an Al alloy and water system, Al and another metal will form a micro-galvanic cell when contacting water due to their difference of electrode potential. As a result, Al takes as the anode and obtains an electron to produce unstable $\text{Al}(\text{OH})_3$ species, but the other metal takes as the cathode where water loses an electron to generate H_2 . The corrosion rate of Al depends strongly on the electrode potential of Al and its contacting metals. Al corrodes fast if electrode potential of Al-Metal is higher. Considering the scenario that Al embedded in liquid GB phases reacts with water. Since Al moves freely in GB phases, Al will separately form micro-galvanic cells with neighboring metals, such as Sn-Al in Al-Ga-Sn eutectic, In-Al in Al-Ga-In eutectic besides Ga-Al. According to calculations^[36], the electrode potentials of Sn-Al, In-Al and Ga-Al are estimated to be -1.53, -1.33 and -1.15 V, respectively. The trend of the dissolution of Al in water will follow the order of Sn-Al > In-Al > Ga-Al. Therefore, the Al-Ga-In alloy exhibits the lowest H_2 generation rate and Al-Ga-Sn alloy exhibits the highest one. Although the Al-Ga-Sn alloys exhibit the highest H_2 generation rates, but their yields are lowest among the three kinds of alloys. So far, the reason why Al-Ga-Sn alloys display the lowest yields is still unknown.

4. Conclusion

Present experiments indicate that Al-water reaction of alloys is promoted by the formation of liquid eutectic phases at Al grain boundary, by which Al atoms of Al grains diffuse to the reaction sites to react with water continuously. The melting point of GB phases affect the reaction temperatures of alloys. Al reacts with water at higher temperatures as the melting points of GB phases in alloys are higher. Compared with 15 wt% Al-Ga-In-Sn and Al-Ga-In alloys, the 15 wt% Al-Ga-Sn alloy exhibits the highest H_2 generation rate and the lowest yield, suggesting that the reaction rates and yields of alloys are not determined by the melting points of GB phases, but by compositions of them. The observed different H_2 generation rates of alloys can be explained using the theory of micro-galvanic cell. Al-water reaction can be controlled by adjusting the compositions of low melting metals in alloys.

Acknowledgements

This work was financially supported by the National Science Foundation of China (Grant No. 51171201) and the National Basic Research Program of China (No. 2010CB631305).

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Figure and table captions

Table 1 Compositions of Al-Ga-Sn alloys obtained using EDX

Table 2 Compositions of Al-Ga-In alloys obtained using EDX

Table 3 Structural components of Al-Ga-Sn alloys calculated by lever rule (wt%)

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.

Fig. 2. Fracture surfaces of (a) and (b) 3 wt% Al-Ga-Sn alloys, (c) and (b) 15 wt% Al-Ga-Sn alloys, (e) and (f) 3 wt% Al-Ga-In alloys, (g) and (h) 15 wt% Al-Ga-In alloys.

Fig. 3. Phase diagram of Al-Ga-Sn alloy^[29].

Fig. 4. DSC curves of (a) Al-Ga-Sn and (b) Al-Ga-In alloys tested at the heating cycle.

Fig. 5. H₂ production curves of Al-Ga-Sn alloys measured at water temperatures of (a) 10 °C, (b) 20 °C, (c) 30 °C, (d) 50 °C, (e) 60 °C, (f) 70 °C.

Fig. 6. H₂ generation rates of Al-Ga-Sn alloys as a function of Ga-Sn content.

Fig. 7. H₂ production curves of (a) 3 wt%, (b) 15 wt% Al-Ga-In alloys measured at different water temperatures.

Fig. 8. H₂ generation rates of Al-Ga-In, Al-Ga-Sn and Al-Ga-In-Sn alloys as a function of water temperatures.

Table List**Table 1**

Sample	Spectrum	Phase	Element (at.%)		
			Al	Ga	Sn
3 wt%	1	G	98.12	1.88	0.00
	2	GB	53.15	3.11	43.74
6 wt%	3	G	97.71	2.29	0.00
	4	GB	21.21	5.67	73.12
8 wt%	5	G	97.36	2.64	0.00
	6	GB	33.32	5.33	61.35
10 wt%	7	G	96.78	3.22	0.00
	8	GB	57.37	5.49	37.14
	9	GB	66.74	31.69	1.57
12 wt%	10	G	96.29	3.71	0.00
	11	GB	28.45	9.62	61.93
	12	GB	30.49	61.84	7.67
15 wt%	13	G	95.79	4.21	0.00
	14	GB	15.53	8.07	76.40
	15	GB	57.95	35.60	6.45

G: Al (Ga) grain, GB: grain boundary phase.

Table 2

Alloy	Spectrum	Phase	Element (at.%)		
			Al	Ga	In
3 wt%	1	G	98.31	1.69	0.00
	2	GB	66.16	1.45	32.39
15 wt%	3	G	95.03	4.97	0.00
	4	GB	18.56	5.67	75.77
	5	GB	50.40	7.06	42.54
	6	GB	62.95	32.03	5.02

G: Al (Ga) grain, GB: grain boundary phase.

Table 3

Sample	primary α -Al	(Al-Sn) eutectic	(Al-Ga-Sn) eutectic
3 wt%	95.61	4.39	0.00
6 wt%	91.43	8.57	0.00
8 wt%	88.63	11.37	0.00
10 wt%	89.91	2.78	7.31
12 wt%	87.85	3.30	8.85
15 wt%	84.82	4.12	11.06

Figure List

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8