Using Grain Refiner Al-3Ti-0.3C to Improve Al-Water Reaction Rate and Yield

DongDong Zhou and Jun Fan*

College of Mechanical Engineering, Xinjiang University, Urumqi, China

Al-Ga-In-Sn alloys with different amounts of a refining agent (Al-3Ti-0.3C) were prepared via atmospheric pressure casting. The microstructures of the resulting alloys were analyzed via X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. With an increase in the Ti content (through Al-3Ti-0.3C) from 0.03 mass% to 0.24 mass%, the grain size of the alloy was refined from 181 to 73 μm . In addition, Al dendrites of several micrometers are observed in the grain of Al alloy.

Our experimental results for the Al-water reaction at different temperatures of water indicate that the hydrogen production rate of the alloy with a Ti content of 0.12 mass% is the highest; in particular, it is about twice that of the alloy without Ti. On further increasing the Ti content, the hydrogen production rate of the alloy-water reaction remained almost unchanged. The hydrogen yield of the alloy decreases from 88% to 66% with an increase in the Ti content from 0.03 mass% to 0.24 mass% at 30°C. However, when the water temperature is increased to 70°C, the hydrogen yield of the alloy increases to more than 90%.

Based on our observations, the mechanism of grain refinement and its effect on the reaction between the alloy and water was proposed.

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1. Introduction

Hydrogen is an efficient and clean source of energy; which is one of the primary fuels used in new hybrid vehicles. The preparation methods for hydrogen mainly include electrolytic water method, microbial decomposition method, and hydro-carbon pyrolysis method.¹⁻²¹⁾ However, in recent years, preparation of hydrogen through Al-water reaction has attracted significant interest from researchers. Al is light-weight, has high specific energy, and is abundant in nature. Furthermore, Al(OH)₃, which is a byproduct of the Al-water reaction, is nonpolluting and can be recycled.^{22,23)}

Under normal conditions, Al does not react with water; however, when the temperature of water is higher than 298 K, the Gibbs free energy G of the reaction between Al and water is less than 0; therefore, according to thermodynamics, at such high temperatures, Al and water can react spontaneously and release heat. Nevertheless, the reaction of Al with water is difficult to achieve because of the dense oxide film that forms on the surface of Al, which hinders further contact between Al and water.²⁴⁾ Therefore, removal of the dense oxide film that forms on the Al surface is key to achieve continuous reaction between Al and water. Considerable research has been conducted on eliminating the oxide film on the surface of Al to promote the reaction between Al and water.²⁵⁻³¹⁾ The primary methods to achieve this include addition of different corrosive media in the aqueous solution, mixing metal and oxide in Al by mechanical alloying, and alloying Al with low-melting metals (Ga, In, Sn, Pb, Bi), among others.

In particular, alloying low-melting metals (viz. Ga, In, and Sn) with Al is an effective method to enable a reaction between Al and water;³²⁾ this is because these low-melting metals can form a liquid Ga-In-Sn (GIS) phase on the surface of the Al grains, which can not only destroy the dense oxide film on the Al surface, but also act as a channel for the

diffusion of Al atoms in Al grains to the interface where the Al-water reaction is occurring, thus promoting a continuous reaction between the Al atoms and water.

Owing to its characteristics of low melting point, fast hydrogen production rate, high hydrogen conversion rate, and easy storage, Al-Ga-In-Sn alloy is suitable for production of hydrogen through its reaction with water. Through a systematic study of the Al-Ga-In-Sn alloy, it was found that its grain size, low-melting metal composition, and other alloy elements affect the Al-water reaction using the alloy.³³⁻³⁷⁾ Among these factors, the grain size of the Al alloy as well as the morphology and distribution of the GIS phase are the key factors affecting the hydrogen production rate and hydrogen conversion rate of the reaction. The results indicate that the smaller the grain size, the smaller the activation energy, and the faster the hydrogen production rate will be.

Ti is an effective element to refine the grain of the Al-Ga-In-Sn alloy. He Tiantian *et al.* showed that when 0.5 mass% pure Ti is added to the Al-Ga-In-Sn alloy, the grain of the alloy changes from columnar to equiaxed.³⁷⁾ In particular, when the Ti content is 1 mass%, the grain size of Al can be refined to 60 μm . However, a high Ti content can inhibit the reaction rate between the alloy and water, reducing the hydrogen yield of the reaction. Furthermore, in practice, because Ti is an expensive metal, a high percentage of Ti in the alloy is also unfavorable in terms of the alloy preparation costs.

Considering this, as an alternative, Al-3Ti-0.3C is often used to refine the grain of the Al alloy. Compared with pure Ti, Al-3Ti-0.3C is more conducive to the stability of heterogeneous nucleating particles in the Al melt; this is because Al-3Ti-0.3C can form stable TiC particles in the melt. Consequently, the TiC particles promote the formation of TiAl₃ particles on the surface of Ti atoms in Al melt.³⁸⁻⁴⁰⁾ In contrast, if pure Ti is added to the alloy, TiAl₃ particles can only form when the Ti content exceeds 0.15 mass% through a peritectic reaction. Thus, a small amount of Al-3Ti-0.3C

*Corresponding author, E-mail: 670203517@qq.com

can effectively refine the Al grain of the alloy. Moreover, the low Ti content in the alloy on using the Al–3Ti–0.3C refiner can also prevent a degradation of the reaction efficiency between the alloy and water.

To the best of our knowledge, thus far, grain refinement using high amounts of the Al–3Ti–0.3C refiner in the Al–Ga–In–Sn alloy, and the hindering effect of the reaction between Al–3Ti–0.3C and water on hydrogen production using the alloy remain unclear. Thus, in this work, the effect of Al–3Ti–0.3C addition on grain refinement of the Al–Ga–In–Sn alloy was studied. In particular, the relationship between the microstructure and interfacial phase composition of the alloy and reaction between Al and water was explored to find the amount of Al–3Ti–0.3C that can suitably refine the grain of the alloy. The microstructure of the refined alloy was studied using X-Ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). Furthermore, the hydrogen production properties of the alloy and water at different temperatures were studied through the drainage gas collection method. Finally, the reaction mechanism between the refined alloy and water was proposed based on our results.

2. Experiment Details

Eight Al alloy ingots of 1 kg were formed using the traditional casting metallurgy method with different amounts of Al–3Ti–0.3C. The weights of the constituent low-melting metals Ga, In, and Sn were set to 3.8 mass%, 1.5 mass%, and 0.7 mass% that of Al for each ingot, respectively. The nominal compositions of the eight alloys are listed in Table 1. As starting materials, 99.99%-pure Al, Ga, In, and Sn are used along with commercial Al–3Ti–0.3C wire. The ingots were melted in a graphite crucible at 750°C in a closed electric furnace. Then, a desired amount of the Al–3Ti–0.3C refiner was added to the melt in the crucible, which was maintained at 750°C for 10 min. To ensure homogeneity, the melt was stirred with a clay-bonded steel ladle for about 30 s, and then cast into a steel mold preheated to 150°C.

The resulting alloy ingots were cut into 2-mm-thick square pieces with a 1-cm side to perform microstructure analysis and Al–water reactivity measurements. The phase compositions of the alloys and reaction products were analyzed via XRD using a Rigaku D/max 2400 diffractometer with monochromated $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda_{\text{K}\alpha} = 0.154056 \text{ nm}$).

The microstructures of the alloys and reaction byproducts were characterized via SEM using an FEI inspect F50 scanning electron microscope with a Quanta 600EDX (EDS) system. To minimize the oxidation of the fractured surfaces of the samples, they were placed in a sample chamber as soon as they were cut.

The equipment used in hydrogen generation experiments was the same as that used in the study by He Tiantian *et al.*³⁷⁾ Experiments were conducted for three different reaction temperatures (i.e., temperature of the water), viz. 30°C, 50°C, and 70°C. For each temperature, 0.3 g of the alloy was added to the reactor, and the test was repeated thrice; the averaged hydrogen generation rates were calculated for the different alloys. Based on these calculations, the yield curves for the cases with a hydrogen yield of less than 80% were selected to obtain the hydrogen generation rates of the samples by calculating the slopes of the selected curves using linear curve fitting. The results reported in this paper are the averages for the three repeated measurements. The temperature of the room in which the experiments were conducted was set to a constant 20°C with a humidity of less than 20%.

3. Results

3.1 X-ray diffraction analysis

Figure 1 shows the XRD spectra of the Al–Ga–In–Sn alloys with different Al–3Ti–0.3C content represented with

Fig. 1 XRD patterns of Al–Ga–In–Sn alloys with different Ti content.

Table 1 Chemical composition of alloys.

Chemical composition of alloys(mass%)					
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.

their equivalent Ti content. Based on the XRD spectra, it is clear that all alloys contain an Al (Ga) solid solution and intermetallic compound In_3Sn , which is consistent with the experimental results reported by He Tiantian *et al.*³⁷⁾ When Al (111) and Al (200) are not refined in the alloy, the ratio of the diffraction peak intensities of the Al (111) to Al (200) crystal planes is about 0.27, which is considerably smaller than that between Al (111) and Al (200) in pure Al, which is 2.128 (PDF Card 040787). This difference in intensity ratios indicates that the growth of Al grains in the alloy without the Al-3Ti-0.3C refiner is directional during solidification, which, in turn, signifies that Al grains easily grow along the grain plane (200). However, when the Ti content in the alloy is more than 0.03 mass%, the ratio of the diffraction peak intensities of Al (111) to Al (200) is about 1.27, which indicates that the grain in the Al alloy with the refiner tends to grow uniformly in all directions.

3.2 SEM observation and EDX analysis

Figures 2 and 3 show the fracture morphology of the Al-Ga-In-Sn alloys with different Al-3Ti-0.3C content and variations in their grain and second phase particle sizes, respectively. Without the refiner, the obtained Al grains are coarse and columnar (Fig. 2(a)) with a width of about 632 μm . However, when the refiner is added to the alloy, the grain of Al changed from columnar to equiaxed. Further-

more, with an increase in the Ti content, the Al grain size gradually decreased. It can be seen from Fig. 3(a) that when the Ti content increases from 0.03 mass% to 0.24 mass%, the Al grain size reduces from about 181 μm to about 73 μm . In contrast, the grain size of the Al with 1 mass% pure Ti is about 60 μm .³⁷⁾ Therefore, compared with pure Ti, Al-3Ti-0.3C refined the grain in the alloy more significantly. In addition, from Fig. 3(b), it can be seen that a large number of bright white grain boundary phases are distributed at the grain boundaries of Al.

The composition of the Al grain and grain boundary phase was analyzed via EDX; these results are listed in Table 2. From the EDX results, it is clear that there is a small amount of Ga in the alloy grains, which is a result of the partial Ga solid solution in the Al lattice. The bright white precipitates contain large amounts of In and Sn, whereas small amounts of Al and Ga. In particular, the atomic ratio of In:Sn is approximately 3:1, indicating that the bright white precipitates are primarily composed of In_3Sn , which is consistent with the results obtained from the XRD analysis.

Figure 4 shows the local enlargement in the fracture morphology of the alloys with different Ti content. As can be seen from Fig. 4, when the Ti content is less than 0.12 mass%, only bright, white GIS phases can be observed at the Al grain boundaries; however, when the Ti content is higher than 0.12 mass%, in addition to bright, white GIS

Fig. 2 The fracture surfaces of Al-Ga-In-Sn alloys with different Ti content (a) 0.00 mass% Ti (b) 0.03 mass% Ti (c) 0.09 mass% Ti (d) 0.15 mass% Ti (e) 0.18 mass% Ti and (f) 0.24 mass% Ti.

Fig. 3 (a) Plot of Al grain sizes with different Ti content in the alloys. (b) Plot of GIS phase sizes with different Ti content in the alloys.

Table 2 Compositions of Al-Ga-In-Sn alloys with different Ti content obtained using EDX.

Composition of 6 mass% Al-Ga-Sn alloys with different Ti contents obtained via EDX.							
Ti Content in Sample	Spectrum	Phase	Element(mass%)				
			Al	Ga	In	Sn	Ti
0.00mass%	1	G	93.07	6.14	0.79		
	2	GB	44.59	4.96	36.24	14.22	
0.06mass%	3	G	97.66	1.86	0.24	0.23	
	4	GB	14.10	4.03	57.92	23.95	
	5	GB	95.53	1.81	1.97	0.69	
0.09mass%	6	G	96.60	3.40			
	7	GB	25.41	4.80	51.44	18.36	
0.15mass%	8	G	97.93	2.07			
	9	GB	34.06	5.22	43.71	17.02	
	10	GB	65.61	2.63	0.81	0.50	30.46
0.18mass%	11	G	96.82	2.45	0.36	0.37	
	12	GB	11.21	4.91	59.04	24.83	
	13	GB	56.94	6.11	2.71	0.74	33.50
G:Al(Ga)grain,GB:grain boundary phase.							

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

Fig. 4 Fracture surfaces of Al-Ga-In-Sn alloys with different Ti content: (a) 0.06 mass% Ti (b) 0.12 mass% Ti (c) 0.18 mass% Ti.

phases, light gray precipitates containing Ti can also be observed at the grain boundaries (Fig. 4(b) and 4(c)). This is because with an increase in the Ti content in the alloy, the amount of precipitate containing Ti also increases. In particular, the EDS results indicate that the Ti content in precipitates increases with an increase in the Ti content in the alloy itself.

From Fig. 4(a), many lamellar (dendritic) structures can be observed in the Al grains. The lamellar structure is only a few micrometers thick. The EDS results confirm that the lamellar structure is Al (Ga) solid solution, which indicates that there are many Al dendrites in the grain of the Al alloy.

3.3 Measurements of Al-water reactivity of alloys

Through our experiments, it was observed that the refined Al-Ga-In-Sn alloy reacted vigorously with water immediately after coming in contact with it, rapidly fragmenting into particles. The higher the temperature of the water, the greater the degree of fractures was. Figure 5 shows the hydrogen production curves for the alloys with different Ti content and different water temperatures. The hydrogen production rate of an alloy can be obtained by linear fitting of the segments whose hydrogen production rate is less than 80% on the

hydrogen production curve. Figure 6 shows the statistical results for the hydrogen production rate and hydrogen generation yields for alloys with different Ti content.

In particular, from Fig. 6(a), it is clear that the hydrogen production rate of an alloy is related to the Ti content in it and the temperature of water. For the same water temperature, when the Ti content in the alloy is less than 0.12 mass%, the hydrogen production rate of the alloy increases with an increase in the Ti content; however, it remains almost unchanged with a further increase in the Ti content. When the Ti content reaches 0.12 mass%, the hydrogen production rate of the alloy reaches the maximum value for a particular water temperature. For example, the hydrogen production rate of the alloy with 0.12 mass% Ti is 540.62 ml/g.Al.min, which is about 2 times of that of Ti-free alloy. Furthermore, for the same Ti content in the alloy, the hydrogen production rate increases with an increase in the water temperature.

The conversion rate of the Al-water reaction is also related to water temperature and Ti content in the alloy (Fig. 6(b)). The conversion rate of the alloy reaches its maximum when the Ti content is 0.09 mass%. In particular, the hydrogen conversion rate is 75% for the alloy without the refiner at

Fig. 5 Hydrogen generation curves of Al-Ga-In-Sn alloys with different Ti content for the following water temperatures: (a) 30°C (b) 50°C and (c) 70°C.

Fig. 6 (a) Hydrogen generation rates and (b) yields of Al-Ga-In-Sn alloys as a function of the Ti content in them.

30°C, which is lower than that of the alloy prepared via arc melting by He Tiantian *et al.*, in which case, it was 90%.³⁷⁾ Furthermore, the hydrogen conversion rate of alloys with Ti content of 0.03–0.15 mass% formed via atmospheric pressure casting is over 80%. However, when the Ti content increases from 0.15–0.24 mass%, the hydrogen yield of the cast alloy decreases from about 82% to 66%. The hydrogen conversion rate of the alloy also increases with an increase in the water temperature. The hydrogen conversion rate of all atmospheric casting alloys is more than 80% at a water temperature of 50°C. At this temperature, when the Ti content in the alloy is increased from 0.03–0.24 mass%, the hydrogen yield of the alloy decreases from 88.74% to 84.32%. Moreover, when the water temperature is increased to 70°C, the hydrogen conversion rate for the Ti-free alloy is 93%. Except for the alloy with a Ti content of 0.09 mass%, the hydrogen conversion rates of the alloys with Ti content are slightly lower than that of the alloy without Ti; however, all of them are above 90%. In addition, considering the experimental results reported by He Tiantian *et al.*,³⁷⁾ for the same Ti content, atmospheric pressure casting alloys have higher

hydrogen production and conversion rates than alloys produced via arc melting.

3.4 Reaction byproducts

The reaction between Al and water remains incomplete when the temperature of the water is 30°C. XRD measurements were used to analyze the phase of the products deposited at the bottom of the reactor after the completion of the reaction of alloys containing 0.06 mass% and 0.24 mass% Ti with water; these results are shown in Fig. 7. It can be seen from the figure that the byproducts of the alloys with Ti content of 0.06 mass% and 0.24 mass% contain α -Al, $\text{Al}(\text{OH})_3$, and In_3Sn phases, and the In_3Sn phases for these two alloys are almost the same. The peak strength of the $\text{Al}(\text{OH})_3$ phase for the alloy with a Ti content of 0.24 mass% is lower than that of the alloy with a Ti content of 0.06 mass%; however, the peak strength of the α -Al phase in the alloy with a Ti content of 0.24 mass% is higher than that of the other alloy, which indicates that more Al participates in the Al-water reaction in the case of the alloy with a Ti content of 0.06 mass% to form the $\text{Al}(\text{OH})_3$ phase.

Fig. 7 XRD patterns of the reaction byproducts for Al-Ga-In-Sn alloys with different Ti content.

4. Discussion

When 0.03 mass% Ti (Al-3Ti-0.3C) is added in Al-Ga-In-Sn alloy, it is found Al grain is changed into equiaxed one and the size of Al grain is reduced compared to that of Al-Ga-In-Sn alloy with 0.00 mass% Ti. In particular, when the Ti content reaches 0.15 mass%, the grain size of the Al alloy is refined to 100 μm . In contrast, when 0.7 mass% pure Ti is added to the Al-Ga-In-Sn alloy, the grain is equiaxed with a size of 108 μm . These observations indicate that a small amount of Al-3Ti-0.3C can refine the Al-Ga-In-Sn alloy more effectively compared with pure Ti. As previously mentioned, this is because the TiC phase in the Al-3Ti-0.3C refiner is beneficial to the formation of a large number of TiAl_3 particles in the Al melt, which increase the heterogeneous nucleation rate of $\alpha\text{-Al}$ and refines the Al grain size. Furthermore, because Al grains grow uniformly in all directions, equiaxed grains are formed. On increasing the Al-3Ti-0.3C content in the alloy, the number of TiAl_3 particles increase, consequently increasing the nucleation rate of $\alpha\text{-Al}$, leading to smaller grain sizes.

The Ti in Al-3Ti-0.3C not only promotes the nucleation of $\alpha\text{-Al}$, but also allows for the accumulation of excess Ti atoms at the liquid-solid interface. Because In and Sn are not soluble in Al, and Ga is only slightly soluble in Al, a large number of Ti, Ga, In, and Sn atoms will accumulate at the liquid-solid interface after solute redistribution. Because these atoms form component undercooling regions in the unsolidified Al melt, $\alpha\text{-Al}$ will grow in the component undercooling region in the form of Al dendrites.⁴¹⁻⁴³ As the Al grains grow, a large number of In and Sn atoms and some Ga atoms at the liquid-solid interface are pushed to the surface of Al grains to form GIS phases at the grain boundary. Furthermore, a small number of In, Sn, and Ga atoms will form GIS phases between Al dendrites because they could not transfer to the grain interface in time, so they stay in the dendrites interfaces.

Compared with the Ti-free alloys, the Al-water reaction with the Ti-containing alloys will inevitably change after grain refinement. At the same water temperature (Fig. 6(a)), with an increase in the Ti content (<0.12 mass%), the hydrogen production rate of the alloy gradually increases

because of the decrease in Al grain size. In particular, the hydrogen production rate of the alloy with a Ti content of 0.12 mass% is about twice that of the Ti-free alloy. Furthermore, the width of Ti-free columnar Al crystal is 632 μm , which is about 5 times the grain size of the Al alloy containing 0.12 mass% Ti (specifically 127 μm). Because of transgranular fractures in Ti-containing alloys, it is impossible to accurately calculate the size of the GIS phase at the interface. However, the trend that the GIS phase area increases with a decrease in alloy grain size means that the GIS phase area increases with an increase in the Ti content of the alloy. The researches^{33,34} show that the hydrogen production rate of the alloy is inversely proportional to the Al grain size and directly proportional to the area of the GIS phase on the surface of Al grain, it can be inferred that the ratio of the hydrogen production rate of the alloy containing 0.12 mass% Ti to the that of the alloy without Ti should be greater than 5. However, based on our results, it is clear that the ratio of hydrogen production rate between the two alloys is less than 5, which indicates that the Ti in the alloys reduces the hydrogen production rate to a certain degree.

On further increasing the Ti content (>0.12 mass%), the Al grain size continues to decrease; however, the hydrogen production rate of the Ti-containing alloys remains unchanged. This further indicates that the hydrogen production rate of Ti-containing alloys is not only related to the Al grain size and GIS phase area at the grain boundaries, but also to the Ti content in alloys. The results of Al-water reaction using the alloy prepared with pure Ti as the refiner also show that Ti in the alloy hinders the Al-water reaction. These experimental results can be explained as follows. Because Ti does not react with water, the soluble Ti in the grain of the Al alloy will occupy some active positions of Al, which will inevitably lead to a smaller effective area of contact between Al and water. During the reaction of the alloy with water, as the Al is consumed, Ti continuously deposits on the surface of the unreacted Al grains, which hinders the diffusion of Al atoms into the GIS phase. Therefore, Ti results in the decrease of the hydrogen production rate and hydrogen yield of the alloy. Furthermore, the analysis of the reaction byproducts indicates that the Al content in the byproducts of the water reaction is higher with an alloy containing high Ti content and vice versa, which confirms our understanding that Ti in the alloy hinders the Al-water reaction. With an increase in the Ti content, the hindering effect of Ti on the Al-water reaction also increases. However, when the Ti content exceeds 0.12 mass%, the hindering effect of Ti on the Al-water reaction is offset by the promotion of grain refinement because of it; therefore, the hydrogen production rate of an alloy with a Ti content greater than 0.12 mass% remains unchanged.

Al grain size is an important factor affecting the Al-water reaction of alloys. The hydrogen production rate and conversion rate of the different alloys differ because of the different grain sizes of alloys prepared via different methods. In particular, when the alloy is prepared via arc melting, the cooling rate during alloy solidification is relatively high; therefore, the grain size of the resulting alloy is small (the width of columnar crystal is 256 μm). However, an alloy prepared via atmospheric pressure casting has a relatively

larger grain size (columnar grain width is 632 μm) because of the lower cooling rate during alloy solidification. Therefore, the hydrogen production rate of alloys prepared via atmospheric pressure casting is lower than of those prepared via arc melting.

When Al–3Ti–0.3C with a Ti content of 0.03 mass% is added to the alloy, the grain of the alloy is equiaxed, which is naturally smaller than that of the alloy without a refiner. Furthermore, the hydrogen production rate of the alloy containing 0.03 mass% Ti at 30°C is higher than that of the alloy without a refiner, because a small amount of Ti in the grain of alloy offers little hindrance to the reaction between Al and water. Nevertheless, at the same temperature (30°C), an increase in the Ti content of the alloy leads to Ti precipitates in the Al grains and grain boundaries, which hinders the reaction between Al and water, gradually decreasing the hydrogen production rate of the alloy.

In addition to the grain size, the temperature of the water used for the reaction is also an important factor affecting hydrogen production rate and hydrogen yield. In general, with an increase in the water temperature ($>50^\circ\text{C}$), the Al–water reaction rate increases. A large number of hydrogen bubbles produced by the Al–water reaction can displace Ti deposited on the surface of the Al grains, which reduces the hindrance Ti offers to the Al–water reaction. Therefore, the hydrogen production rate and hydrogen yield of the alloys increase with an increase in the water temperature. When the water temperature is 70°C (Fig. 6(b)), the hydrogen yield for the different alloys reaches more than 90%, which indicates that the hindering effect of Ti on the hydrogen production rate and yield of alloys becomes weak above this temperature.

5. Conclusions

The effect of different amounts of Al–3Ti–0.3C as a refiner in Al–Ga–In–Sn casting alloy on the alloy's microstructure and Al–water reaction were studied. The following conclusions were drawn:

Compared with pure Ti, Al–3Ti–0.3C had a more remarkable grain refinement effect.

The grain of the alloys containing Al–3Ti–0.3C was equiaxed with lamellar dendrites in the grain. When the equivalent Ti content in the alloy was higher than 0.12 mass%, precipitates containing Ti appear at the grain boundary. The amount of precipitates increases with increase in the Ti content.

When the temperature of the water used for the Al–water reaction is low ($<50^\circ\text{C}$), the hydrogen production rate using the Al–Ga–In–Sn alloy decreases with an increase in the Ti content. However, with an increase in the water temperature, the hindering effect of Ti on the reaction between the alloy and water is weakened, leading to a hydrogen production rate of more than 90%.

The hydrogen production rate of the alloy with a Ti content of 0.12 mass% is the highest. Increasing the Ti content beyond this amount leads to an increase in the hindering effect of Ti on the reaction; however, the hydrogen production rate of the alloy remains almost unchanged. Thus, based on our results, the optimum amount of Al–3Ti–

0.3C to add to the Al–Ga–In–Sn alloy for enhanced hydrogen production rate and yield is 2.4 mass%.

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