Rare Metal Materials and Engineering
Volume 46, Issue 9, September 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(9): 2428-2432.

ARTICLE

Effects of Preparation Parameters and Alloy Elements on the Hydrogen Generation Performance of Aluminum Alloy-0 °C Pure Water Reaction

Chang Ying [1, 2, 3], **Liu Bei**[1, 2, 3], **Wang Huihu** [1, 2, 3], **Dong Shijie** [1, 2, 3]

[1] Hubei Provincial Key Laboratory of Green Materials for Light Industry, Wuhan 430068, China; [2] Collaborative Innovation Center of Green Light-weight Materials and Processing, Hubei University of Technology, Wuhan 430068, China; [3] School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan 430068, China

Abstract: Aluminum (Al) alloys with gallium (Ga) and indium (In) were prepared via mechanical alloying technology. The hydrolysis reaction between the Al alloys and pure water was studied to analyze the hydrogen yield evolution. The results obtained by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy show that Ga and In elements mainly exist in the alloy in the forms of dissolution and precipitated phases, respectively. The dissolution of Ga and In can improve the hydrogen yield of Al alloy by enhancing the activity of hydrolysis reaction. Moreover, the quantity and distribution of precipitated phase determined by ball milling time directly influence the hydrogen yields, and the Al alloy with appropriate number and uniform-distributed precipitated phase can react with 0 °C pure water to produce 1132.8 mL/g hydrogen.

Key words: aluminum alloys; mechanical alloying; aluminum alloy-water reaction

There are many proposed methods for the development of new effective and ecologically sustainable hydrogen sources. One of the prospective methods is hydrogen generation from water by means of aluminum (Al)-water reaction. However, the mechanisms that enable the reaction to begin and to proceed remain unclear, as does the question whether the reaction can be controlled. We are sure that Al mobilization via different attempts and approaches is a good idea. According to current literatures [1-13], processes and methods have been developed to disrupt the formation of alumina film that acts as a protective barrier on the Al surface, halting or preventing the Al water reaction. Possible routes to Al activation are as follows: 1) amalgamation (amalgam treatment). However, this method is not acceptable because of the mercury toxicity and relatively low hydrogen generation rate[1-3]; 2) reaction of Al oxidation using alkaline aqueous solutions. However, the reaction is relatively slow, despite the required high temperature, and caution is necessary for working with strong alkaline solutions[4-6]; and 3) use of micron and ultrafine particles with high specific surfaces. The shortcoming of this method is the requirement for high reaction start temperatures (more than 40 ℃) and relatively low reaction rates[7, 8]. In addition, the low melting point metals such as gallium (Ga) and indium (In) are also added to Al for the sake of surface activation promotion[9-15]. To our knowledge, no studies have been reported on the Al alloy-water reaction under low temperature conditions (0 °C). In the present research, we investigated the reaction between Al alloy and pure water at 0 ℃. Using the hydrogen yield as the assessment index, the orthogonal test was adopted to optimize the preparation process of Al alloy. Different Al alloy samples were prepared by ball milling, and the effects of preparation parameters and alloy elements on the activity and the hydrogen evolution performance were studied.

1 Experiments

The untreated starting materials were Al (particle size≤74 μm,

---

Received date: September 15, 2016
Foundation item: National Natural Science Foundation of China (51004046, 51075129); Wuhan Youth Chenguang Program of Science and Technology (2013070104010016); Middle-aged and Young Program of Educational Commission of Hubei Province (Q20101409)
Corresponding author: Dong Shijie, Professor, School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan 430068, P. R. China, E-mail: dongsjsj@ mail.hust.edu.cn

99.99 wt%), Ga (99.8 wt%), and In (particle size≤74 μm, 99 wt%). The powders were mixed in an argon-filled glove box, and then milled in special ceramic pots filled with an argon atmosphere by a planetary ball miller. The rotation speed of the miller was 500 r/min, and the weight ratio of ball to powders was 20:1. To investigate the effects of ball milling time on the reactivity of the alloy, the ball milling time was variable at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 h, but the optimal Ga and In content remained the same. The reaction of Al powders with the 0 ℃ pure water was conducted in a special glass reactor[16]. Batch-type experiments were carried out, where Al powder was placed first within the reactor, followed by adding 30 ml water. The reaction then started spontaneously. The temperature of the water was measured by a Chromel/Alumel thermocouple. The total volume of the generated hydrogen (the hydrogen yield) was measured using the drainage method (Fig.1). To study the process in isothermal conditions, a glass reactor filled with water was placed with a thermometer. Milled Al powders were characterized by a scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS), and an X-ray diffractometer (XRD) with CuKα radiation (Si internal standard method).

2 Results and Discussion

2.1 Analysis of orthogonal test

2.1.1 The choice of orthogonal test factors and levels

We selected an Al-Ga-In alloy system, and the orthogonal test method was introduced. It has several advantages including the evenly distributed points for data collection, the minimized trials for a complete analysis, and convenient range and variance analysis. The three influencing factors (Ga content, In content and ball milling time) are denoted by the characters from A to C, respectively. Each factor has three levels indexed from 1 to 3, which denotes the chosen values of the operating parameters. Different levels and factors in the orthogonal test are listed in Table 1.

2.1.2 Method of orthogonal test

The hydrogen yield of the Al alloy-water reaction was selected as the observation index of the orthogonal test. The selected orthogonal table of $L_9 3^3$ (Table 2), including three factors and three levels, is adopted to arrange nine cases, the minimum number for a complete and systematic analysis.

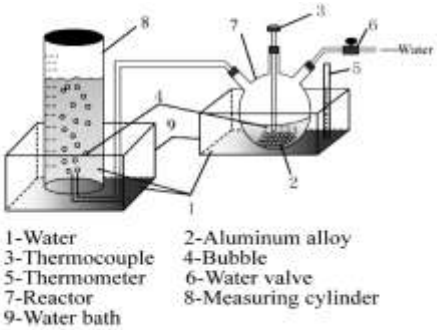


Fig.1 Schematic of the experimental installation for measuring hydrogen generated by the Al-water reaction

2.1.3 Analysis of orthogonal test results

Table 3 presents influences of the multi-factors on the hydrogen yield. *R* represents significance level of the factors, and *K*1 to *K*3 represent values of level 1 to 3. According to the orthogonal test theory, the factor with a larger *R* is more important than other factors. Similarly, the level with a larger *k* is superior to other levels. Hence, the order of the influences on the hydrogen yield is A, B and C. The optimal combination for the largest hydrogen yield is A2B1C1.

2.2 Effects of Ga and In on the reactivity and the hydrogen yield

According to the Al-Ga phase diagram[17], the biggest solid solubility of Ga in Al is 20 wt%, which indicates that Ga atoms (5 wt%, 3 wt%, and 2 wt%, see Table 1) can completely dissolve into pure Al. Furthermore, the atomic radius of Ga is 1.83 angstroms, and that of Al is 1.82 angstroms. The small difference of atomic radius between the two elements will result in a lower lattice distortion. Therefore, the Ga atom can dissolve into the Al lattice in the form of atomic replacement. Fig.2 shows

Table 1 Factors and levels of the orthogonal test

Levels	Factors		
	A: Ga content/ wt%	B: In content/ wt%	C: Ball milling time/h
1	2	2	6
2	3	3	12
3	5	5	24

Table 2 Orthogonal table of $L_9 3^3$ and hydrogen yield (mL/g) of Al alloys

Case	A	B	C	Hydrogen volume/mL g^{-1}
1	1	1	1	1015.7
2	1	2	2	1014.8
3	1	3	3	696.5
4	2	1	2	961.4
5	2	2	3	973.9
6	2	3	1	1009.5
7	3	1	3	759.5
8	3	2	1	661.7
9	3	3	2	641.9

Table 3 Analysis of the results using the range method for the hydrogen yield (mL/g)

Parameters	A	B	C
*K*1	2727	2736.6	2686.9
*K*2	2944.8	2650.4	2618.1
*K*3	2063.1	2347.9	2429.9
*k*1	909	912.2	895.6
*k*2	981.6	883.5	872.7
*k*3	687.7	782.6	810
R	293.9	129.6	85.6
Order	A＞B＞C		
Optimal combination	A2B1C1		

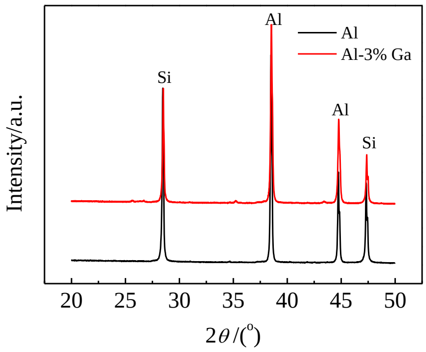


Fig.2 X-ray diffraction patterns of alloy powders after 12 h ball milling

the XRD patterns of 12 h ball milled Al-Ga alloy. There is no Ga peak, which demonstrates Ga has dissolved in the Al matrix.

Meanwhile, the solubility of In in Al is small (0.01~0.05 wt%) according to the Al-In phase diagram[18]. However, the activation performance of Al-In alloy improves with the increase of In content in the range of 0.01~0.04 wt%. When the content is higher than 0.1%, the excess In exists in the form of precipitated phase, which could further accelerate the hydrogen evolution corrosion of the Al alloy[19, 20]. In this experiment, the smallest In content (2 wt%, Table 1), far higher than the equilibrium solubility of In in Al, implies a large number of In precipitated phases existing in Al, which has been proven by the appearance of the In diffraction peaks (Fig.3).

2.3 Effects of the precipitated phase on the reactivity and the hydrogen yield

Activation elements of the alloy mainly exist in the forms of solid solution or precipitated phase (more than in solution), which is likely to cause defects on the surface oxide film. Owing to the potential difference between matrix and precipitated phase, this will inevitably form tiny corrosion cells in the alloy-activation medium and result in splitting of surface oxide film. The activation process is as follows[21, 22]:

(1) The added alloy elements simultaneously dissolve with the Al matrix.

$$\text{Al (In, Ga)} \rightarrow \text{A1}^{3+} + \text{In}^{3+} + \text{Ga}^{3+} + 9e^- \quad (1)$$

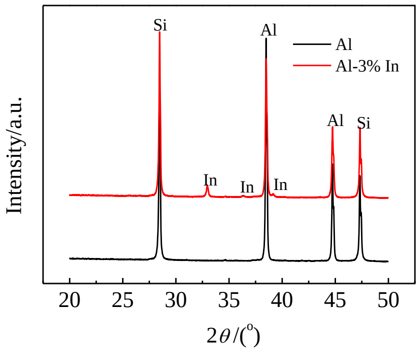


Fig.3 X-ray diffraction patterns of alloy powders after 12 h ball milling

(2) Because the balanced electrode potential of Ga and In dissolved in Al is more positive than that of Al alone[23], the Ga and In ions are reduced to produce Ga and In atoms through ion exchange reactions and are redeposited on the surface of the alloy.

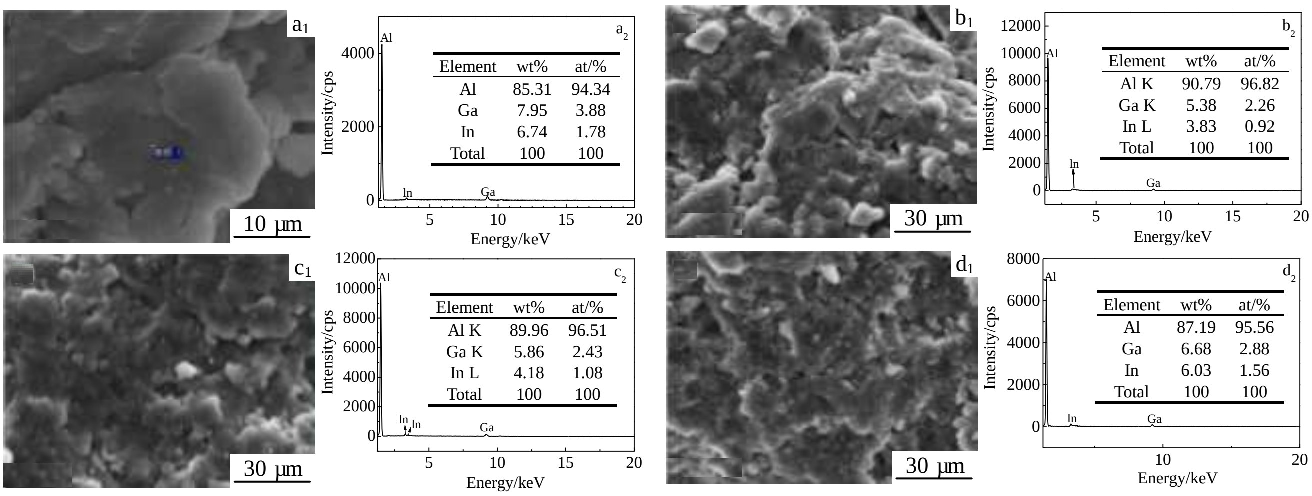
$$2\text{Al} + \text{In}^{3+} + \text{Ga}^{3+} \rightarrow 2\text{Al}^{3+} + \text{In} + \text{Ga} \quad (2)$$

(3) The deposited alloy elements mechanically separate from the surface passivation film, resulting in loss of the passivation film (this process occurs simultaneously with the second step).

In contrast, according to "the second-phase preferential dissolution" mechanism originating from the "dissolution-redeposition" mechanism[24], the precipitated phase would dissolve preferentially and play a key role in the initial stage of corrosion. That is, the matrix becomes exposed and activated by the dissolved precipitated phase during the reaction process. Because of the restriction from the surface passivation film, the horizontal spread ability of corrosion is limited, but the vertical spread ability of corrosion is effectively unconstrained. Thus, the electrochemical corrosion also proceeds without limits beneath the surface of passivation film, which increases the speed of corrosion development and results in the excellent hydrogen evolution performance of the alloy.

Fig.4 are SEM images and EDS analysis of the alloys with different precipitated phase contents. The relatively high content of Ga and In (Fig.4a_2) originates from EDS result of the small white point (Fig.4a_1). This indicates that the activation elements (Ga and In) form the precipitated phase in this area. Figs. 4b_1~d_1 are SEM images. Fig.4b_1 presents a few small white points, and the largest number of small white points is shown in Fig.4d_1. The amount of small white points in Fig.4c_1 is between that of Fig.4b_1 and Fig.4d_1, indicating the contents of Ga and In in these samples (corresponding to Fig. 4b_1, c_1 and d_1) successively increase, which was also confirmed by Figs.4b_2~d_2). Correspondingly, the hydrogen yields of these samples are 641.9, 1132.8, and 1009.6 mL/g, respectively, which suggests that the hydrogen yield would not increase with the increase of precipitated phase (the quantity of small white points). However, according to previously mentioned analysis, the precipitated phase has a beneficial effect on hydrogen production from the Al alloy-water reaction. It might seem paradoxical, but it tells us that: in order to produce a largest amount of hydrogen, it is necessary to maintain the appropriate amount of the precipitated phase, neither too much nor too little.

As shown in Fig.4b_1, the reduced activation energy caused by a few small white points would result in the slow Al alloy-water reaction and a small hydrogen yield. With the increase of the precipitated phase (the number of small white points), uniform corrosion is likely to form on surface of the alloy when the alloy possesses a homogeneous distribution and appropriate precipitated phase amount (Fig.4c_1). The preferential solubility reactivation process of the precipitated phase would continue and produce a largest amount of hydrogen. However, with too much precipitated phase (Fig.4d$_1$), the alloy is likely to dissolve so quickly that the violent hydrolysis process would cause incomplete Al alloy-water reaction, resulting in a relatively low hydrogen yield.



a$_2$

Element	wt%	at/%
Al	85.31	94.34
Ga	7.95	3.88
In	6.74	1.78
Total	100	100

b$_2$

Element	wt%	at/%
Al K	90.79	96.82
Ga K	5.38	2.26
In L	3.83	0.92
Total	100	100

c$_2$

Element	wt%	at/%
Al K	89.96	96.51
Ga K	5.86	2.43
In L	4.18	1.08
Total	100	100

d$_2$

Element	wt%	at/%
Al	87.19	95.56
Ga	6.68	2.88
In	6.03	1.56
Total	100	100

Fig.4 SEM images and EDS analysis of alloys with different precipitated phase contents: (a) small white point analysis result; (b, c; d) selected area analysis results

2.4 Effects of ball milling time on the reactivity of the alloy

The ball milling time also has a key influence on the reactivity of the alloy. According to Table 3, prolonged ball milling time can decrease the hydrogen yield. However, Fig. 5 shows that the hydrogen yield increases with milling time increasing and reaches a maximum at about 7 h, but slightly decreases after that, which suggests it is very important for the hydrogen yield to select an appropriate ball milling time, neither too long nor too short. As the ball milling time is less than 3 h, the corresponding low hydrogen yield indicates the shorter ball milling time for mixed powders is a disadvantage. With an increase of the ball milling time, the mechanical alloying process of mixed powders is gradually completed, Ga and In would become uniformly distributed in the Al matrix in the form of white pitting, and the pitting of metal Al would become the electrochemical activity point to enhance the reactivity of Al. Therefore, the hydrogen yield substantially increases in the range of 3~7 h milling time. After 7 h, with further increase of milling time, the additive metals uniformly distributed in Al matrix begin to partly dissolve in Al crystal lattice and transform into solid solution. Owing to the decrease of the second phase (precipitated phase or the pitting) distributed in Al matrix, the Al reactivity is slightly reduced, causing a slight decrease in the hydrogen yield[14]. Therefore, the optimum ball milling time of 6 h derived from the result of the orthogonal test should be increased to 7 h.

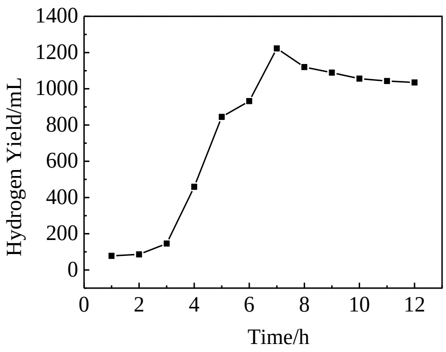


Fig.5 Hydrogen yield curve against the ball milling time

3 Conclusions

1) The Ga and In elements in Al alloy, which can react with pure water, mainly exist in the forms of dissolution and precipitated phase, respectively.

2) The dissolution of Ga and In can enhance the activity and improve the hydrogen evolution performance of Al alloy, which is consistent with the dissolution-redeposition mechanism. The precipitated phase of Ga and In can accelerate the hydrogen evolution corrosion, which is consistent with "the second-phase preferential dissolution" mechanism.

3) The quantity and distribution of the precipitated phase directly impacts the hydrogen yield, and Al alloy with homogeneous distribution and appropriate precipitated phase amount can react with 0 ℃ pure water to produce 1132.8 mL/g of hydrogen, which will be beneficial to the hydrogen preparation by aluminum-water reaction in

cold regions.

References

1 Bennett J E, Pinnel M R. *Journal of Materials Science* [J], 1973, 8: 1189

2 Gu B S, Gong L, Yang P Y. *Rare Metal Materials and Engineering* [J], 2014, 2: 429

3 Shmelev V, Nikolaev V, Lee J H *et al. International Journal of Hydrogen Energy* [J], 2016, 38: 16664

4 Liang J, Gao L J, Miao N N *et al. Energy* [J], 2016, 113: 282

5 Jung C R, Kundu A, Ku B *et al. Journal of Power Sources* [J], 2008, 175: 490

6 Soler L, Candela A M, Macanas J *et al. International Journal of Hydrogen Energy* [J], 2010, 35: 1038

7 Shmelev V, Yang H, Yim C. *International Journal of Hydrogen Energy*[J], 2016, 33: 14562

8 Shaytura N S, Laritchev M N, Laritcheva O O *et al. Current Applied Physics* [J], 2010, 10: S66

9 Wang H Z, Leung D Y C, Leung M K H *et al. Renewable and Sustainable Energy Reviews* [J], 2009, 13: 845

10 Ziebarth J T, Woodall J M, Kramer R A *et al. International Journal of Hydrogen Energy* [J], 2011, 36: 5271

11 Ilyukhina A V, Ilyukhin A S, E I Shkolnikov. *International Journal of Hydrogen Energy* [J], 2012, 37: 16382

12 Razavi-Tousi, S S, Szpunar J A. *Journal of Alloys and Compounds* [J], 2016, 679: 364

13 Wang H, Chang Y, Dong S *et al. International Journal of Hydrogen Energy* [J], 2013, 38: 1236

14 Wang H, Lu J, Dong S *et al. Materials Transactions* [J], 2014, 55(6): 892

15 Wang F, Wang H, Wang J *et al. Transactions of Nonferrous Metals Society of China* [J], 2016, 26(1): 152

16 Rosenband V, Gany A. *International Journal of Hydrogen Energy* [J], 2010, 35: 10898

17 Zivkovi D, Balanovic L, Manasijevic D *et al. Thermochimica Acta* [J], 2012, 544: 6

18 Hansen M, Anderko K. *Constitution of Binary Alloys, 2nd Edition*[M]. New York: McGraw-Hill Book Company, 1958

19 Emamy M, Keyvani A, Mahta M *et al. Journal of Materials Science and Technology* [J], 2009, 25: 95

20 Venugopal A, Raja V S. *British Corrosion Journal* [J], 2004, 31: 318

21 Munoz A G, Saidman S B, Bessone J B. *Corrosion Science* [J], 2002, 44: 2171

22 Breslin C B, Friery L P. *Corrosion Science* [J], 1994, 36: 231

23 Lemieux E, Grolleau A, Hogan E *et al. Corrosion* [J], 2002, 58: 16

24 Reboul M C, Gimenez P H, Rameau J J. *Corrosion* [J], 1984, 40: 366

制备工艺参数与合金元素对铝（合金）一水（0 ℃）反应产氢性能的影响

常 鹰[1,2,3]，刘 备[1,2,3]，王辉虎[1,2,3]，董仕节[1,2,3]

（1. 绿色轻工材料湖北省重点实验室，湖北 武汉 430068）

（2. 绿色轻质材料与加工湖北工业大学协同创新中心，湖北 武汉 430068）

（3. 湖北工业大学 材料与化学工程学院，湖北 武汉 430068）

摘 要：通过机械合金化技术制备了含镓和铟的铝合金，研究该合金与纯水之间的水解反应来考察氢产率的变化。X射线衍射、扫描电镜与能谱分析结果表明，镓和铟元素分别主要以溶解与沉积相的形式存在于合金之中。溶解的镓和铟通过增强水解反应活性来提高铝合金的产氢率。此外，由球磨时间决定的沉积相的数量及分布也会直接影响合金的产氢率，具有均匀分布及合适数量沉积相的铝合金能与0 ℃水反应产生1132.8 mL/g的氢气。

关键词：铝合金；机械合金化；铝水反应

作者简介：常 鹰，男，1976 年生，博士，教授，湖北工业大学材料与化学工程学院，湖北 武汉 430068，E-mail: cy0025@ mail.hbut.edu.cn