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論　文

アルミニウム廃材による水からの水素生成

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Hydrogen Production from Water by Use of Waste Aluminum

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Abstract

Waste aluminum is recycled and reused as aluminum raw material. Another way of recycling is possible for aluminum. It decomposes water at room temperature to produce hydrogen and aluminum hydroxide under certain conditions. The present paper describes preliminary results of a study on factors affecting the rate of hydrogen production using pure aluminum and Al-Mg alloy. The results showed : (1)Cold-rolling is effective to enhance the reaction, indicating that defect structures play important roles, (2)Alloying magnesium to aluminum is much more effective to increase the reaction rate than the cold-rolling of pure aluminum, (3)An important factor to affect the reaction rate appears to be corrosion cracking patterns through formation of fresh surfaces and/or active sites.

1. Introduction

Growing use of fossil energy gives rise to a serious environmental problem such as the green-house effect, acid precipitation, photochemical smog and so on. This has been recognized as a world wide problem to be solved urgently. There should be many

optional solutions for this concern. One of the most convincing solutions is to develop new energy sources other than fossils, such as solar energy, magma energy and so on.

Another point of importance is to recycle materials to keep the environment free from wastes and/or the natural resources under human control. Hydrogen energy system is much attractive from this view point, because the reaction product is only water which causes no environmental problem and can be recycled to produce hydrogen. To produce hydrogen, however, water should be decomposed with electrochemical and/or thermal reactions at the expense of energy.

It is well known that some metals decompose water to evolve hydrogen as a reaction product. Among these metals, aluminum is one of the most commonly used material. The reaction rate, however, is considerably slow in the presence of surface protective layers. In another word, aluminum and its alloys react fairly fast with water in the lack of the surface protective layers. Hydrogen produced is the fuel in the hydrogen energy system and the another reaction product, aluminum hydroxide, can be used for other purposes.

It is a well established fact that the reaction of aluminum with water is considerably enhanced by amalgamation[1]. The factors affecting the enhancement, however, are not fully understood. In this respect, we studied kinetics and mechanisms of the water decomposition by amalgamated aluminum. This paper describes preliminary experimental results on the kinetics of the decomposition reaction.

2. Experimental

2. 1. Apparatus and materials

The apparatus used was quite simple as shown in Fig. 1. It consisted of a glass reaction vessel of 100 cm^3 in volume. It was connected with "Tygon" to a measuring cylinder of 200 cm^3 to measure the gas evolved. Another reaction product, precipitates, was analyzed with a conventional thermoanalysis system.

Aluminum samples used are listed in Table 1. Sample No. 1 was purchased from Hokusei Aluminum Co. and was delivered as plate. The others were prepared at the

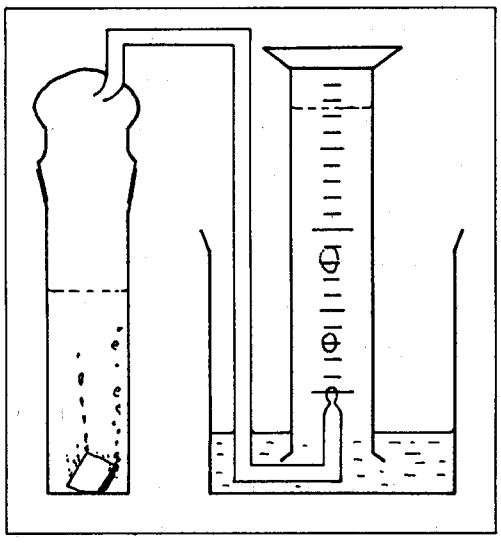

Fig. 1 Schematic diagram of the experimental apparatus.

Table 1. Summary of characteristics of samples.

No.	Sample	Purity (wt%)	Size (mm^3)	Weight (g)	Treatment
1	Al*	99.99	10×10×0.5	0.12987	as-received
2	Al	99.99	10×10×0.75	0.20387	as-received
3	Al	99.99	10×10×1.35	0.36246	cold-rolled (32.5%)
4	Al	99.99	10×10×0.75	0.19680	cold-rolled (62.5%)
5	Al-Mg	Mg : 5.16	10×10×0.85	0.21401	cold-rolled (57.5%)

*The sample of No. 1 was delivered from Hokusei Aluminum Co.
*The extent of cold-rolling is define as (Hi-Ho) /Hi, where Hi and Ho are the thickness of a plate before and after cold-rolling, respectively.

Faculty of Engineering of Toyama University and offered as plate from Professor Tada. Some of them were cold-rolled to examine the effects of deformation. The extent of the cold-rolling appears in the Table 1.

A mercury solution was prepared from reagent grade mercury, zinc and sodium hydroxide. Namely, 0.2 g of zinc powder was mixed with 5.5 g of mercury in a beaker, in which 20 ml of sodium hydroxide solution (45wt%) was added subsequently.

2. 2. Procedures

A sample plate was immersed in the mercury solution for about 15 seconds. Subsequently a cross section and a radial section of the plate were made contact with the mercury for several seconds. Next, the plate was quickly washed with distilled water and put in the reaction vessel which had been filled with about 30 ml of distilled water.

Gas evolution was measured as a function of time at room temperature (22－28 ℃). The another product, precipitates, was characterized with thermogravimetric analysis (TGA) and differential thermal analysis (DTA) by using Rigaku TG-DTA (8101 BH). Prior to the analyses, the precipitate was dried at 120 ℃. The operation conditions of TGA and DTA were : temperature ramp was 10 ℃/min, argon flow rate 50 cm^3/min, the reference material Al_2O_3 (5.87 mg).

3. Results and discussion

3. 1. Gas evolution

Figure 2 is an example of the time course of the gas evolution for Sample No. 1.

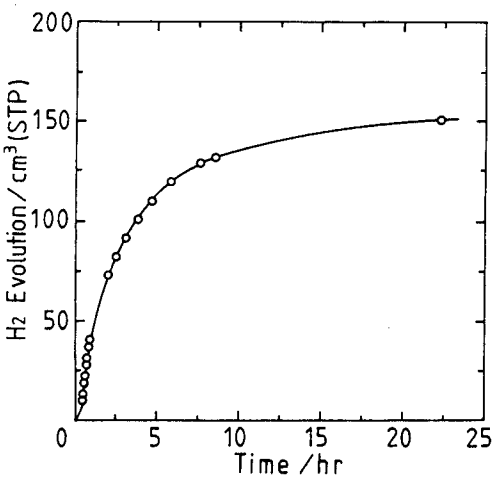

Fig. 2. Evolution of hydrogen gas by the Sample No. 1.

As seen in the figure, after a short induction period, the reaction rate increased with time for a while and then slowly decreased to zero. The gas evolved amounted to 150.3 cm^3 (STP) in 22.2 hr.

The reaction taken place should be either of

$$2Al + 4H_2O \rightarrow Al_2O_3 \cdot H_2O + 3H_2 \quad (1)$$

$$2Al + 6H_2O \rightarrow Al_2O_3 \cdot 3H_2O + 3H_2 \quad (2)$$

For both of the equations, one gram-atom of aluminum produces 1.5 mol of hydrogen and the heat of reaction is about −200 kcal /mol[2]. These equations suggest that Sample No. 1 which consisted of 4.81×10^{-3} gram-atom of aluminum produces 161.6 cm^3 (STP) of hydrogen. This is quite near to the observed amount of hydrogen. On account that hydrogen solubility in water is fairly large as 2.14 cm^3 (STP) per 100 ml of water, the difference between the observed and estimated should be due to solution of hydrogen molecules in water.

At the initial stage of the reaction, gas bubbles were formed around the cross and radial sections having been amalgamated. These parts changed to flake-like structures and incresed in thickness about 10 times in 20 minutes. The sample plate eventually crumbled to colloidal particles and completely disappeared at the end of the reaction to form white precipitate. Photograph 1 is an electron micrograph showing the surface state of a sample plate picked up during the reaction. Photograph 2 shows the preci-

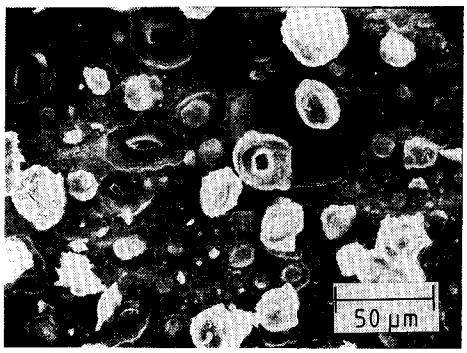

Photo. 1. Observation of corrosion surface by a scanning electron microscope.

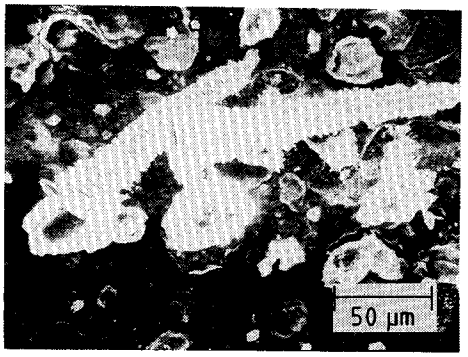

Photo. 2. Reaction products by the decomposition of water.

pitates. In the former, there can be seen many pit-holes on the surface. These observations strongly suggest that the reaction proceeds via electrochemical processes.

In the present case, there are two metallic elements on the surface and hence the reactions as

$$Al^{3+} + 3e^- \rightarrow Al \quad (3)$$

$$Hg_2^{2+} + 2e^- \rightarrow 2Hg \quad (4)$$

are plausible. The standard potentials (E^0) are -1.66 and 0.792V for Eqs. (3) and (4), respectively[3]. Namely, aluminum acts as anode and mercury as cathode. Accordingly, the corrosion reaction should be written as

$$Al \rightarrow Al^{3+} + 3e^- \quad (5)$$

$$3H_2O + 3e^- \rightarrow 3OH^- + (3/2)\ H_2 \quad (6)$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3. \quad (7)$$

The reaction kinetics was examined with three typical rate laws commonly observed for oxidation of metals,

$$V = k\ t \quad (8)$$

$$V = (2\,k\,t)^{1/2} \quad (9)$$

$$V = \alpha + \beta\ \log(t), \quad (10)$$

where V is the amount of hydrogen evolved, and k, α and β are constants for a given material. The parabolic and logarithmic plots are shown in Fig. 3, which indicates the hydrogen evolution over Sample No. 1 obeys the logarithmic law, Eq. (10). The linear rate law is not valid as seen in Fig. 3.

Figure 4 shows the hydrogen evolution over the sample from No. 2 to No. 4, where the results for Samples No. 1 and

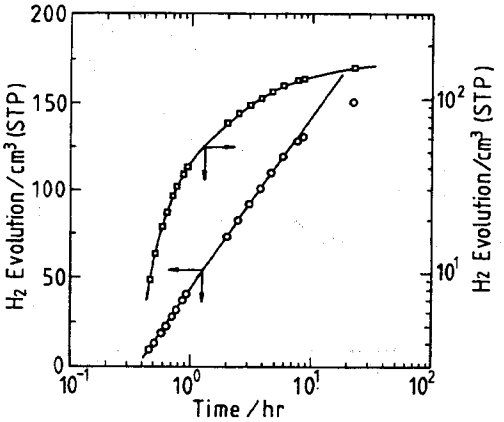

Fig. 3. Applicability of some rate laws for the Sample No. 1.

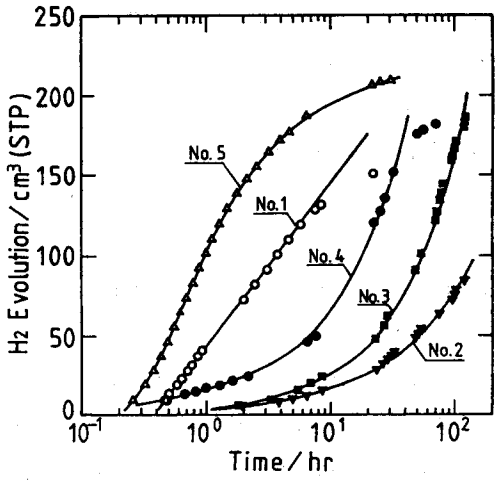

Fig. 4. Examination of the applicability of the logarithmic rate law. Numbers in the figure describe the sample number.

5 are also shown for comparison. It is obvious that the hydrogen evolution over Samples No. 2, 3 and 4 do not obey the logarithmic law mentioned above. This is also true for Sample No. 5. As seen in the figure, the rate of reaction increased with increasing extent of cold-rolling. These sample plates behaved differently from Sample No. 1. Namely, the flake-like disintegration did not take place, but they broke into small blocks. Blocking was almost completed in 2, 1 and 1/2 hours for Samples No. 2, 3 and 4, respectively. These observations indicate that the cold-rolling causes to increase the reaction rate as well as the blocking rate.

With respect to the kinetics, any of the rate laws mentioned above were not valid for sample from No. 2 to 5. On account of blocking behavior, therefore, we examined a kinetic expression on the analogy of the autocatalytic reaction[4] : a nucleus is supposed to act as an active site for the reaction. The rate of nucleation is generally described as

$$dN/dt = \alpha t^{\beta-1}, \quad (11)$$

where N is the number of the active sites, and α and β are constants. By integration

$$N = (\alpha/\beta) t^{\beta}. \quad (12)$$

Consequently, the rate of hydrogen evolution is expressed as

$$dV/dt = kN = (k\alpha/\beta) t^{\beta}, \quad (13)$$

where k is the rate constant. Integration of Eq. (13) and sequent rearrangement lead to the expression as

$$\log(V) = \log(A) + B \log(t), \quad (14)$$

where $A = k\alpha/(\beta B)$ and $B = \beta + 1$. Figure 5 shows the plots for the samples from No. 2 to 4. Three of them resulted in straight line. The results, however, are not simple. The exponent, β, was evaluated as -0.29, -0.17 and -0.38 for the samples No. 2, 3 and 4, respectively. It appears to be a complex function of the extent of cold-rolling. This is also true for the constants, k and α.

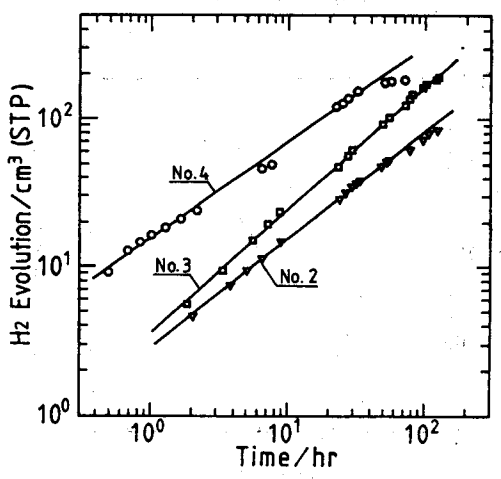

Fig. 5. Log(V) vs. Log(t) plots for Samples No. 2, 3 and 4.

The hydrogen evolution over the Al-Mg alloy, Sample No. 5, did not obey any of the rate laws described above. It is noteworthy that the hydrogen evolution was fastest among the samples used in

the present study, indicating that magnesium doped in aluminum acts as an active center for this reaction.

Those observations indicate that the kinetics and mechanisms are not identical even for a given material prepared differently. Presence of dopants and/or alloying causes further changes in reaction rate and mechanism. This phenomenon will be studied in detail and reported in futrue.

3. 2. Thermal analyses of precipitates

The precipitates were analyzed with TGA and DTA. Figure 6 shows an example of the analyses, for Sample No. 1. Prior to the analysis, the precipitates were dried at 120 ℃ for 53 hours. The TG curve shows initial gradual decrease in weight below 120 ℃. This is considered due to adsorbed water, because similar feature is commonly observed for many oxide powders. Above this temperature, sharp decrease took place till 340 ℃. The sample weight decreased further with slower rate till 450 ℃. In the DTA curve, there appear peaks at 180 and 256 ℃, and a shoulder around 340 ℃. All of them indicate endothermic reaction. These peaks and a shoulder well correspond to the steps in the weight loss. They will be denoted as the first, second and third step, respectively. The weight losses were about 3% in the first step, 15.9% in the second one and 5.9% in the third one. The total weight loss amounted to 24.8% for this sample.

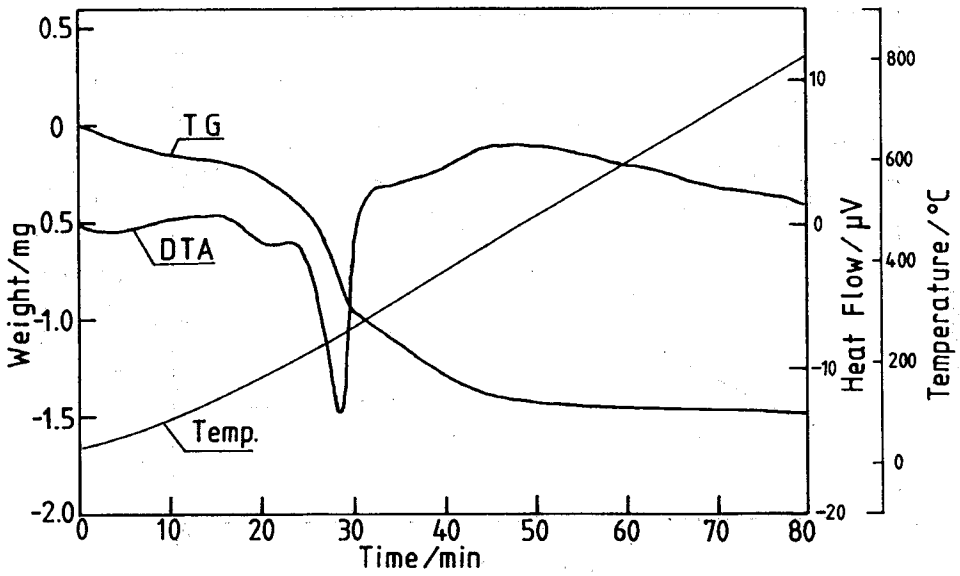

Fig. 6. Thermal analysis of white precipitate obtained after the reaction.

On account of the products in the reaction schemes described above, the precipitate should be aluminum hydroxide. Several kinds of aluminum hydroxide are known as[5] ;

$Al_2O_3 \cdot H_2O$ ($AlO(OH)$)
- Boehmite ($\gamma - Al_2O_3 \cdot H_2O$)
- Diaspore ($\alpha - Al_2O_3 \cdot H_2O$)

$Al_2O_3 \cdot 3H_2O$ ($Al(OH)_3$)
- Gibbsite ($\gamma - Al_2O_3 \cdot 3H_2O$)
- Bayerite ($\alpha - Al_2O_3 \cdot 3H_2O$)

Boehmite and diaspore are dehydrated at about 450℃ to form Al_2O_3. Gibbsite decomposes to boehmite at 250℃ and then to $\gamma - Al_2O_3$ about 500℃. According to the stoichiometry of the above processes, boehmite and diaspore lose their weight amounting to 15.0%, and the trihydrates do 34.6%. The observed loss for Sample No. 1, however, was 24.8%, being inconsistent with both of these values.

To examine this discrepancy, reagent grade $Al(OH)_3$ was analyzed with TG and DTA. Figure 7 shows an example of TG and DTA curves. Heat absorption took place at 216, 259 and 318℃. These peaks were accompanied with weight losses of 4%, 22.0 % and 7.9%, respectively. Except the initial weight loss below 120℃, the total loss amounted to 33.9%. This is consistent with the estimated loss of 34.6%. Although the weight loss of $Al(OH)_3$ was different from that of Sample No. 1, there was a similar feature in the DTA curves. Namely, most strong peaks appeared about 250℃ which

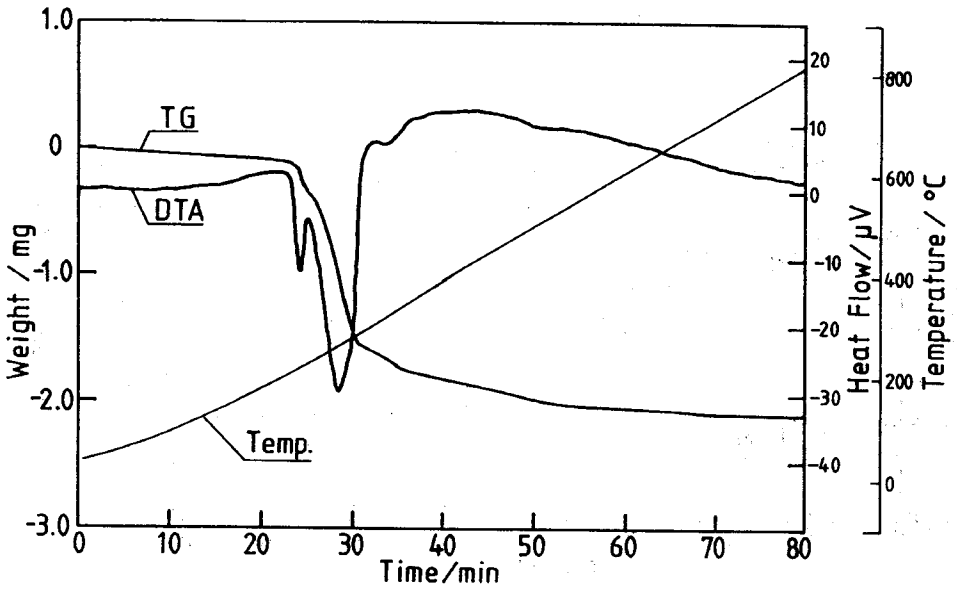

Fig. 7. Thermal analysis of aluminum hydrate ($Al(OH)_3$).

was accompanied with an absorption peak at lower temperature and one at higher temperature, although these satellite peaks appeared at different temperatures between the two. This kinds of peak shift are commonly observed for a given sample material prepared under different conditions. Hence it is considered that the sample precipitates principally consisted of $Al(OH)_3$, but was partially in an amorphous state, because the sample conditioning for thermal analysis appears to be insufficient for aging to crystallize freshly precipitated amorphous aluminum hydroxide. It is also plausible that the precipitates was a mixture of monohydrate and trihydrate, giving the somewhat different features in TG and DTA curves from those of $Al(OH)_3$ and the intermediate value in weight loss between 15% for monohydrate and 34.6% for trihydrate. This point should be studied further with other analytical techniques.

4. Summary

Aluminum is one of the most common metals used in a variety of practical materials. Under certain conditions, it decomposes water to produce hydrogen. This study is concerned with utilization of aluminum wastes to produce a clean energy source, hydrogen, and aluminum hydroxide and/or alumina which can be also utilized for various purposes. The present preliminary study showed :

1. The reaction products are only hydrogen and aluminum hydroxide(s) for pure aluminum.
2. The reaction rate is sensitive to cold-rolling : the larger the extent of cold-work, the higher the reaction rate. This indicates that defect structures play important roles.
3. Alloying magnesium into aluminum is much more effective to increase the reaction rate than cold-rolling of pure aluminum.
4. Both the cold-rolling and alloying appear to cause changes in the reaction mechanisms, but its detail is an open question.
5. An important factor affecting the reaction rate is corrosion cracking patterns. It appears that the corrosion cracking patterns are important for both the reaction rate and mechanism through affecting the nature of fresh surface or active sites.

Acknowledgments

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