



# Mechanism of Corrosion of Activated Aluminum Particles by Hot Water



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## ABSTRACT

Mechanism of corrosion in aluminum particles by hot water treatment for hydrogen generation is evaluated. The aluminum powder was activated by ball milling for different durations, which modified size and microstructure of the particles. Open circuit potential test was carried out to elucidate different stages of the reaction. Tafel test was used to explain the effect of ball milling and growth of hydroxide layer on corrosion of the particles. Surface, cross section and thickness of the grown hydroxide on the aluminum particles were studied in a scanning electron microscope. The corrosion potential of the aluminum powders depends on microstructure of the aluminum particles, growth of the hydroxide layer and a change in pH because of cathodic reactions. The hydrogen production test showed that a deformed microstructure and smaller particle size accelerates the corrosion rate of aluminum by hot water, the effect of the deformed microstructure being more significant at the beginning of the reaction. Effect of growth of the hydroxide layer on corrosion mechanism is discussed.

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## 1. Introduction

Reaction of aluminum and water can be used as a source for hydrogen. The reaction produces 1.24 litre of hydrogen per 1 g of aluminum. The major difficulty for this reaction is the passivation of aluminum surface by a protective oxide/hydroxide layer that retards the reaction and may stop the reaction to progress.

Extensive researches have been accomplished to promote reaction of aluminum with water. These primarily include either direct ball milling of monolithic aluminum powders [1–4] or addition of selective catalysts to aluminum powders during ball milling, such as low melting point (LMP) metals like Ga, In, Bi, Hg and Zn [5–10], water soluble salts like NaCl and KCl [7,8,11–15] and ceramic powders like  $\text{Al}_2\text{O}_3(\alpha)$ ,  $\text{Al}_2\text{O}_3(\gamma)$ ,  $\text{TiO}_2$ , C,  $\text{SiO}_2$  and  $\text{Al}(\text{OH})_3$  [15–24]. Because an increase in temperature makes the kinetics of the reaction faster, most of the above mentioned work conducted the reaction with hot water.

The corrosion behaviour of aluminum at room temperature has been studied extensively in the past, however, less attention has been paid to understand the corrosion mechanism of aluminum by use of hot water. In addition to hydrogen generation, there have

been few major aspects for which the reaction of aluminum and hot water has been a subject of interest. Corrosion of aluminum alloys used in fuel cladding in reactors was studied using hot water treatment [25–30]. On the other hand, the corrosion of aluminum with hot water was also studied as a method to improve adhesion strength of polymer coatings to aluminum surface [31–33]. The corrosion of aluminum by hot water forms a porous hydroxide layer on the surface of aluminum, which remarkably increases strength of the bonding between aluminum and polymer coatings. The reaction of aluminum with hot water was also investigated to manipulate the oxide/hydroxide layer on the surface of aluminum components used in electronic industries [34].

The above mentioned applications led scientists to gain a good insight into the mechanism of the reaction of bulk aluminum with hot water. R.S. Alwitt [35], W. J. Bernard et al. [36], W. Vedder et al. [37] and B. R. Baker et al. [38] conducted methodical investigations dedicated to understand corrosion behaviour of aluminum samples by use of hot water.

On the other hand, in spite of the numerous studies on hydrogen generation through the corrosion of ball milled aluminum particles by water, a thorough evaluation of the reaction mechanism is yet to be understood. The main focus of the previous studies on hydrogen generation from Al-water reaction was to activate aluminum in a way to generate higher amount of hydrogen in a short time period. To knowledge of the authors, no electrochemical route has been performed till date to understand the reaction between aluminum

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particles and hot water and how ball milling promotes the reaction.

This study aims to fill the gap between the remarkable interest in production of hydrogen from corrosion of ball milled aluminum particles by hot water and a deeper understanding on the mechanism of the reaction. We conducted the reaction at 80 °C as this is the optimum temperature for operating PEM (proton exchange membrane) and many other types of fuel cells. We neither manipulated pH of the water nor added any second phase powder to promote the kinetics of the reaction; so that the study purely considers the reaction mechanism of aluminum with hot water and effect of ball milling on the reaction kinetics. We examined four different powders (as received, 1 h, 7 h and 19 h milled), however in the present study, we focus on comparison of the as received and 19 h milled powders for the reason that both as received and 19 h milled particles show equiaxed morphology and structurally non-laminated. Thus without interference of other variables, we can investigate effect of particle size and deformed microstructure on hydrogen generation and reaction mechanism.

## 2. Experimental

### 2.1. Ball Milling

Aluminum powder, 99.8% purity (MFCD00134029) was procured from Alfa Aesar®. We used Stearic acid (97% purity, Fisher Scientific-AC17449-0010) as process control agent and mixed 3 wt% of it with the aluminum powder prior to milling. A planetary ball mill (Torrey Hills- ND2L) with stainless steel cups (285 ml capacity) and balls (28 of 16 mm and 6 of 18 mm diameter) milled the powders in an argon (Ar) atmosphere. Ball to powder ratio was 30:1 and the mill speed was maintained at 200 RPM for durations of 1, 7, and 19 hours (h). The ball milled powders were exposed to air after milling process.

### 2.2. Hydrogen Measurement

The hydrogen measurement set-up was under air atmosphere. We added 2 g aluminum powder into an Erlenmeyer flask contained 200 ml distilled water at temperature of 80 ± 3 °C with a constant stirring rate of 120 rpm. The produced hydrogen gas passed through a desiccant (CoCl<sub>2</sub>) to absorb moisture, and then an ADM2000 flowmeter measured the flow with an accuracy of 0.1 ml/min. The flowmeter was connected to the computer and the ADM Trend software acquired the data. We measured the flow for the first 1–2 h of the reaction for each sample and then normalized the results for 1 g aluminum powder. The hydrogen yield curves vs. time were obtained by integrating the flow data over time. We did not continue measuring hydrogen flow after 2 h of the reaction because the collected data was sufficient to investigate effect of microstructure on the rate of Al-water reaction.

We obtained a baseline curve by measuring the flow from 200 ml distilled water at temperature of 80 °C with a constant stirring rate of 120 rpm with no aluminum powder added. The baseline data was subtracted from the data obtained from the reactions to ensure that the measurements did not include the effect of water moisture or expansion of air in the flask during heating.

### 2.3. Scanning Electron Microscopy

A Hitachi SU6600 field emission scanning electron microscope (SEM) examined the surface and cross section of the powders. We added a small amount of the powder to a conductive carbon resin powder, mixed and mounted it. We polished the mounted samples by abrasive grinding papers from 600 to 2000 grit followed by additional grinding with diamond pastes of 3 and 0.04 μm. An Oxford

Instruments Nordlys Nano detector was used as an integral part of the microscope to collect the electron backscattered diffraction (EBSD) patterns generated from the samples tilted at an angle of 70° relative to the microscope stage. The SEM for the EBSD characterisation was operated at an acceleration voltage of 10–30 kV, depending on the grain size of the sample. Applying a misorientation cut-off of 15°, the grain size of the samples was determined by a post processing module Channel 5-Oxford Instruments. We obtained size of over 500 grains to calculate the average grain size for each of the samples. The area weighted average (Eq. 1) was calculated as the average grain size:

$$D_s = \frac{\sum n_i D_i^3}{n_i D_i^3} \quad (1)$$

where  $D_i$  is the size of the grain  $i$ ,  $n_i$  is number of grains with size  $D_i$  and  $D_s$  is the surface weighted average.

The Microstructure Measurement software calculated thickness of the hydroxide layer on the surface of the particles by analyses of SEM images from cross section of the particles. The thickness data point for each sample was obtained by arithmetic averaging of 30–70 measurements.

### 2.4. Open Circuit Potential and Tafel Measurements

A Gamry potentiostat (interface 1030) obtained the open corrosion potential (OCP) of the powders vs. saturated calomel electrode (SCE) with a step size of 1 sec. We pasted the aluminum powders to microscope slides using conductive carbon paint (LEIT-C™) and applied a 0.95 cm<sup>2</sup> area by PortHoles electrochemical sample masks (Gamry3 M Model 470). We used a solution of 2.84 gr sodium sulfate in 200 ml distilled water (equivalent of 0.1 mol/lit) as the electrolyte, which was conductive and neutral. For the Tafel tests, the potential was swept in the positive direction from a cathodic potential of –250 mV<sub>OCP</sub> to an anodic potential of 250 mV<sub>OCP</sub>. The scan rate for Tafel measurements was 0.3 mV/sec. The situation for the OCP and Tafel experiments was similar to that of the hydrogen measurement tests (stirring rate: 120 rpm, temperature: 80 °C and distilled water volume: 200 ml).

## 3. Results and Discussion

### 3.1. Effect of Ball Milling on Aluminum Particles

Fig. 1 shows the cross section of an as received aluminum particle and aluminum particles milled for 1 h, 7 h and 19 h. The equiaxed cross section of the as received particle changed to a rectangular shape after 1 h milling. Previous works established that at the initial stages of milling, impacts deform the equiaxed particles to flattened flakes [4,39]. A transverse cross section of a flake results in a rectangular shape, similar to what is depicted in Fig. 1(b). Further deformation up to 7 and 19 h significantly decreases the particle size of the aluminum particles. We measured particle size of the powder by a laser particle size analyser, which showed a decrease in particle size from an initial size of 192 μm of the as received sample to 74 μm and 44 μm for the 7 h and 19 h ball milled powders, respectively.

In addition to the effect of ball milling on shape and size of the particles, the 7 h milled particle has a laminated structure (Fig. 1(c)). This laminated structure is produced by cold welding of flattened aluminum particles [40]. The interlayer spaces between the layers of the 7 h milled particles increase the available surface for the reaction [4]. Fig. 1(d) shows that further milling up to 19 h eliminates the laminated structure of the particles.

Fig. 2 shows EBSD patterns of an as received aluminum particle and aluminum particles milled for 1 h and 7 h. Different colors are

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