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ORIGINAL PAPER

Enhancing aluminum corrosion in water

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Abstract For small particles of aluminum (<60 µm), a measurable percentage of the aluminum (>5%) is observed to corrode before passivation occurs at moderate temperatures (>50 °C) in de-ionized water within 1 h. Ball-milling of the aluminum powders with aluminum oxide or water soluble salts results in a significant increase in both the rate of corrosion and the extent of corrosion before passivation. The resulting release of hydrogen gas is of commercial interest for portable hydrogen supply systems. This paper investigates the effect of temperature increase, pH shift, and change of surface area during milling, on the corrosion rate of aluminum powders in water.

Keywords Aluminum · Ball-milling · Corrosion · Hydrogen

1 Introduction

With the current concern with global warming, air pollution, and diminishing reserves of fossil fuels, there has been increased emphasis on transitioning to a hydrogen economy. Hydrogen is made at large scale today (mostly from natural gas) for use in chemical processes such as oil refining and ammonia production [1]. About 1% of U.S. primary energy use (~5% of U.S. natural gas use) goes to hydrogen production for chemical applications [2]. However, if hydrogen is to be widely used as a future energy carrier, storage will be needed to meet time-varying demands for fuel and allow for mobile energy sources. Methods of interest include compression, liquefactation, physisorption, metallic hydrides, and complex hydrides [3]. The most common storage solution for small systems is currently pressure cylinders and industry has set a target of a cylinder with a gravimetric storage density of 6 mass% and a volumetric storage density of 30 kg/m^3 [4].

Aluminum being a reactive metal will readily form aluminum hydroxide when placed into water with a resulting release of H_2 gas [5]. Looking at a mass balance equation we can calculate that aluminum could have an equivalent storage density of 11 mass%, well above current storage targets. However in practice aluminum is almost always found with a protective Al_2O_3 oxide layer covering the bulk material due to reaction with oxygen in the atmosphere. This layer is non-soluble and prevents the Al–water reaction. In near neutral pH pure water systems, aluminum is reported to form various aluminum hydroxides depending on water temperature and pressure all of which form a passivating layer that grows to at most a couple of microns thickness before the reaction stops [6]. For this reason aluminum has not traditionally been viewed as a practical source for hydrogen generation.

In the 1990s, Asok Chaklader discovered that after milling aluminum with aluminum oxide the resulting mixture when submerged in water at neutral pH ranges would produce significantly more hydrogen than the same aluminum without ball milling [7]. Beside hydrogen, water vapor is the only other gas evolved which is beneficial in Proton Exchange Membrane (PEM) type fuel cells. The lack of other trace gases like S, CO, or CO_2 which can poison fuel cells, is also an advantage over hydrogen from steam reforming natural gas. The aluminum hydroxide byproduct is also non-toxic and can be handled safely. This gives a significant advantage over other Al–water split systems which rely on sodium hydroxide as a catalyst [8].

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Further work by Czech [9] has established conditions under which high % yields are produced in time frames of commercial interest, but an investigation into the changes that milling produces in aluminum is needed to better understand this system. With the milling step currently being both time consuming and energy intensive, it is important to understand if surface area needs to be optimized or if corrosion rates are controlled by pH and temperature changes. To answer this question the surface area of the aluminum powder after ball milling with alumina will be determined and effect on corrosion rate plotted. The effect of both pH and temperature shifts on un-milled aluminum powder determined and compared with ball milled systems.

2 Experimental procedures

Sample description and preparation; A solid disk is 1.5 cm in diameter stamped from aluminum foil of 99.99% purity and used during electrochemical tests. Aluminum powder has an average particle diameter from 23 to 48 μm (ALCOA grade 101 typically 99.7% Al), and is either used loose in water when hydrogen is being collected or it is compacted in a die to 350 kg cm^{-2} and the resulting pellet used in an electrochemical cell. Ball milled (BM) samples are Al powder hand mixed with Al_2O_3 powder at equal weights unless specified otherwise using a glass rod (ALCOA A-16SG, 99.8% calcined alumina), and then ball-milled for 15 min in a SPEX 8000 high energy shaker mill with 38 g of alumina balls. Typically only 1–2 g of powder are milled at a time and then for electrochemical tests 1 g of powder is pressed to 350 kg cm^{-2} into a pellet of similar dimensions to the solid disk. The Al powder may also be ball milled with KCl at equal weights and is referred to as washed Al when the salt has been removed by multiple immersions in cold water and filtration. Corrosion of loose powder was measured by capturing evolved hydrogen in a water filled inverted graduated cylinder, the downward displacement of water indicating the amount of evolved hydrogen with approximately 5 mL initially lost to clear the tubing between beaker and cylinder.

A Princeton Applied Research potentiostat model 273A was used for electrochemical work with a standard three electrode corrosion cell using a Ag/AgCl reference electrode. All potentials are graphed versus standard hydrogen electrode (SHE). The corrosion cell was jacketed and a variable temperature controller circulated water around the cell to maintain cell temperature to within 0.5 °C of set point. Potentiodynamic tests were run at 0.5 mV s^{-1} from −1 V versus open circuit upward, and potentiostatic tests run at +200 mV versus SHE. XRD of reacted powders and disks was used to determine reaction end products ($Al(OH)_3$ and AlOOH) and check for salts after washing. BET was used for surface area measurements with nitrogen gas after heating the powders under a vacuum overnight.

Most test solutions used for hydrogen evolution were de-ionized water which showed a pH shift from 7 to over 9 if the reaction occurred in small (<100 mL) volume of water during which a significant (>500 mL) amount of hydrogen was evolved. To replicate this pH during some of the electrochemical tests a 0.01 M Borax ($Na_2B_4O_7 \cdot 10H_2O$) solution was used which will buffer close to a pH of 9. In hydrogen evolution tests looking at increased pH, a solution of NaOH was titrated into the water until the desired pH was reached.

3 Results and discussions

When looking at ball-milled (BM) samples in water above 50 °C the hydrogen evolution is fairly rapid and can be measured by the displacement of water by H_2 in an inverted graduated cylinder. From the gas evolution rate an aluminum corrosion rate can be calculated and the percent of aluminum that has reacted in the sample known. The two reactions seen depending on the water temperature are:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \tag{1}$$

$$2Al + 4H_2O \rightarrow 2AlOOH + 3H_2. \tag{2}$$

In both cases the cathodic and anodic reactions are:

Cathode: $6H^+ + 6e^- \rightarrow 3H_2$

Anode: $Al \rightarrow Al^{+3} + 3e^-$.

The difference between Eq. 1 and Eq. 2 is that Eq. 2 consumes less water to produce the same amount of hydrogen which might be important in portable applications where weight is important. Equation 2 also forms a different aluminum hydroxide which as discussed later can be more passivating. From the above equations we can also calculate that each mole of aluminum if fully reacted will produce 3/2 mole of hydrogen, or 1,354 mL of hydrogen per gram of aluminum. This allows us to estimate the extent of aluminum corrosion from the amount of hydrogen captured.

As can be seen from Fig. 1, over 70% of the aluminum can be corroded within 1 h. In this case the aluminum was milled with a water soluble salt (KCl), and the presence or absence of the salt in the case of washed samples has minimal impact upon the corrosion rate [9]. When reacted in a small volume of water an increase in solution pH is seen followed by a rapid spike in evolved hydrogen and temperature. The temperature and pH spikes were not originally seen when using a surplus of water (>1 L), and became more pronounced with reduced water volume. For

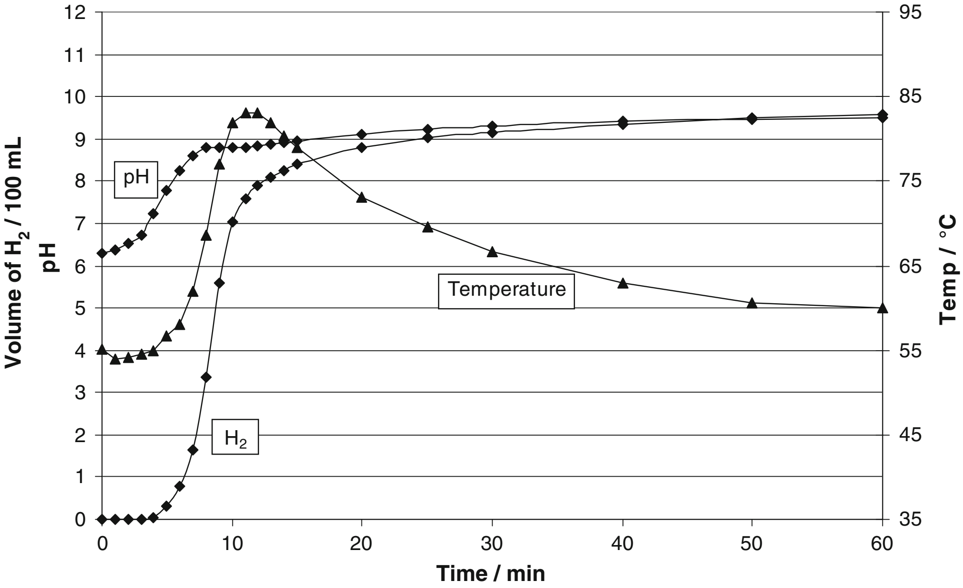


Fig. 1 Volume of hydrogen gas produced with time from 1 g of Al ball milled with 1 g KCl placed into 30 mL of water at 55 °C, with corresponding temperature and pH curves

this reason, it was suggested that local micro-environments of high pH and temperature might be formed within the deformed aluminum. These pockets might form corrosion cells similar to pitting that would alter the overall corrosion of the sample beyond what would be expected from the increased surface area the ball milling would create.

3.1 Effect of pH

First compare the potentiodynamic scans of aluminum disks and BM Al pellets in water (Fig. 2) and a Borax solution (Fig. 3). In both solutions the ball milled sample is more reactive by two orders of magnitude, but in water there is almost a 500 mV difference in open circuit potential between the Al disk and the BM sample. Tests run in water with BM powder showed an increase in pH to around 9, so Fig. 3 uses a 0.01 M Borax solution which will buffer at pH 9. The open circuit potential of the Al disk drops to the −900 mV SHE seen for the BM sample in water, while the BM sample shows only a slight decrease to below −1 V. This suggests that the BM sample may see a surface pH change long before a pH shift is observed in the bulk solution. The overall corrosion rate of the aluminum was not seen to increase however.

In Fig. 4 it can be seen that the corrosion rate for a loose aluminum powder at pH 10 falls between that seen for two independent runs at pH 7 and doesn't increase until pH 11 which is much higher than seen during evolution tests such as Fig. 1. From these tests we conclude that the alkalization of solution occurring from hydrogen evolution may shift the open circuit potential the aluminum sits at, but does not account for the increased reaction rate seen with ball milled samples.

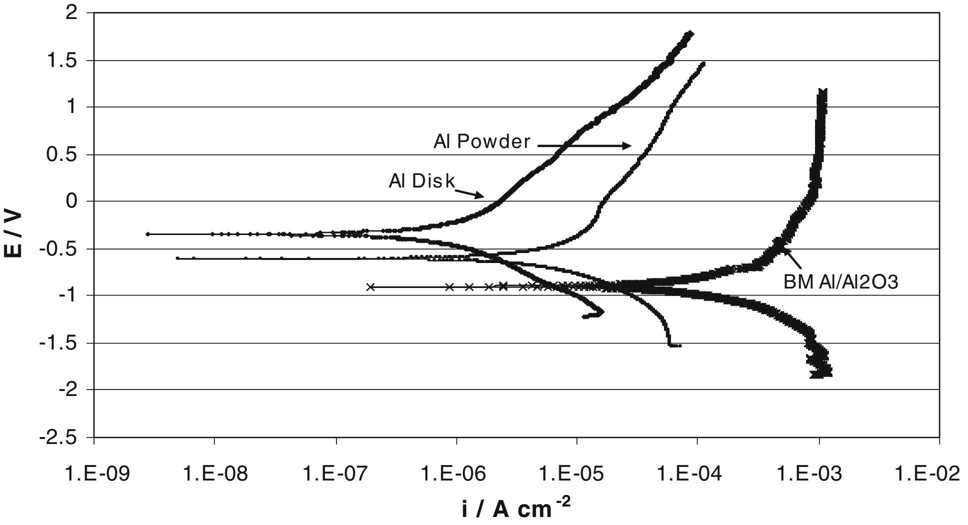


Fig. 2 Polarization curves of an Al disk, Al powder pellet, and Al powder that was ball milled with Al_2O_3, in water at 25 °C

Fig. 3 Polarization curves of an Al disk and a BM Al/Al_2O_3 pellet in a 0.01 M Borax solution at 25 °C

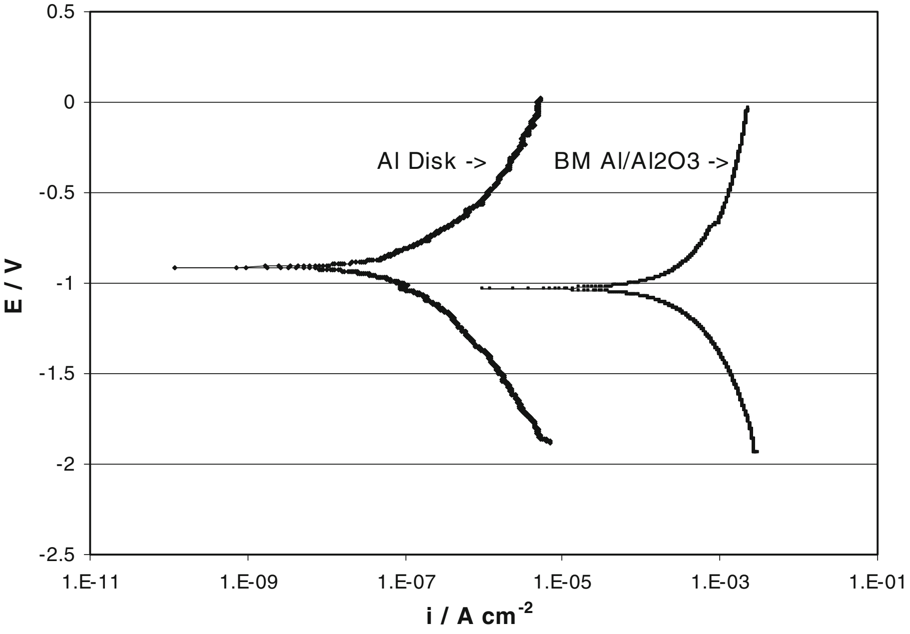
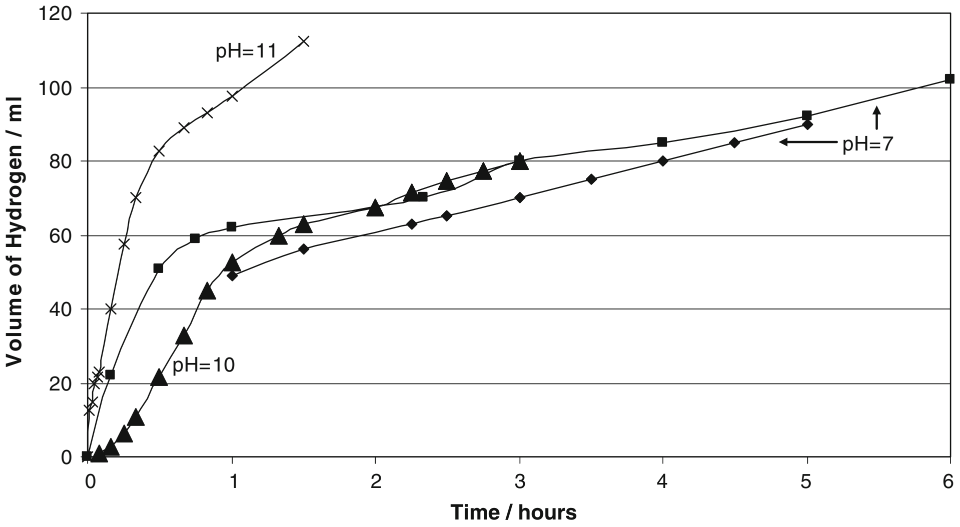


Fig. 4 Hydrogen evolution from 0.5 g of Al powder in 70 °C water, solution pH of 10 and 11 from the addition of NaOH



3.2 Effect of temperature

The exothermic nature of the aluminum water reaction generates heat as seen in Fig. 1, which will in general increase reaction rates. Looking at Fig. 5 we see an increase of roughly 10 times in the corrosion current going from 25 to 50 °C. We see this same increase in Fig. 6 which shows the current as a function of time for an aluminum disk held at +200 mV SHE potential in a 0.01 M Borax solution. Every 12 h the temperature was increased 15 °C from 10 to 85 °C. Initially the current decreased logarithmically as a hydroxide layer grew on the surface of the disk, but after the initial 12 h the surface stabilized and current tended to remain fixed at each new temperature. A noted change started 8 h into the 70 °C period and a dramatic drop in rate was observed at 85 °C. The logarithmic drop indicates a change in the surface layer affecting the corrosion rate. Subsequent XRD tests (Fig. 7) showed a layer of AlOOH had grown at this temperature where the previous film of $Al(OH)_3$ present at lower temperatures was too thin to resolve with XRD. This indicates that while increasing temperature accelerates the corrosion it does so only below 85 °C, higher temperatures switch the reaction product and a more passivating film is grown.

Figure 7 shows XRD peaks from samples held in the borax solution for 24 h at 55 and 85 °C. At 55 °C only the aluminum peaks are seen and any surface layer is too thin to be detected. Prior investigation by Czech [9] indicates that this initial layer is $Al(OH)_3$, other researchers [10] reported the outer layer of growth to be $Al_2O_3(3H_2O)$. The

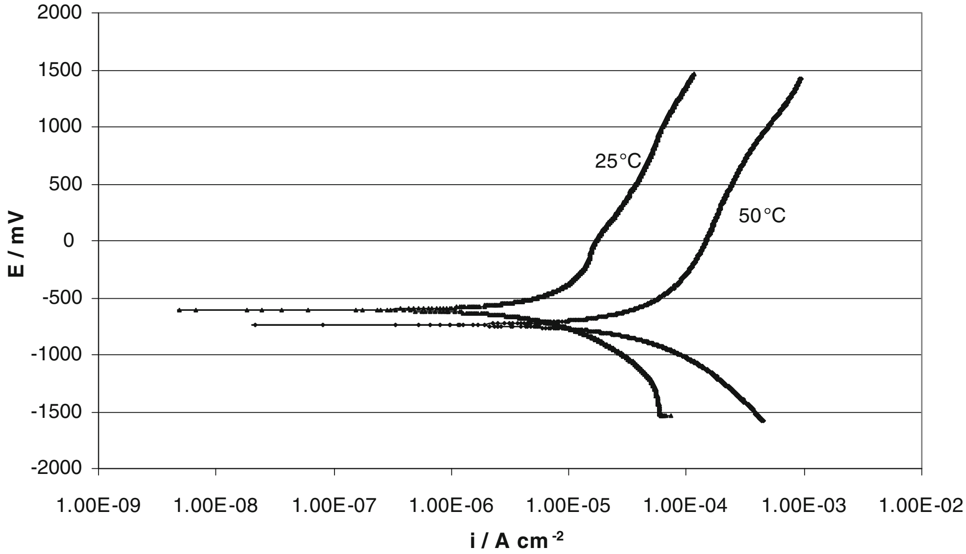


Fig. 5 Polarization curves for Al powder pellets in water at 25 and 50 °C

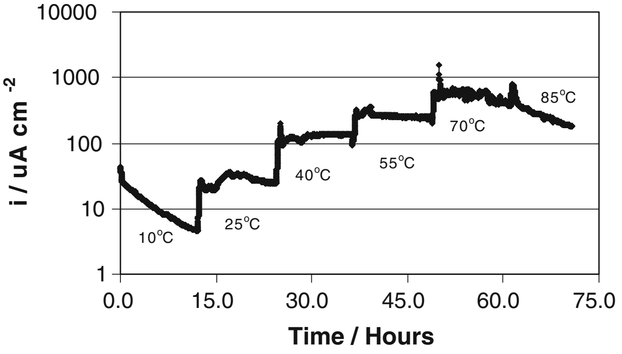


Fig. 6 Current with time for Al disk in a 0.01 M Borax solution held at +200 mV for 12 h at each temperature from 10 to 85 °C

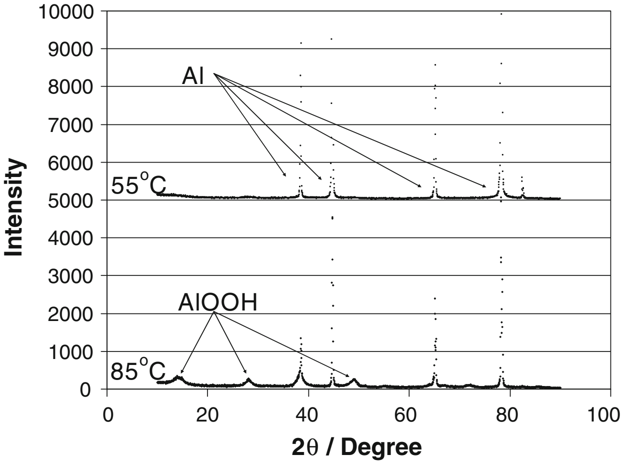


Fig. 7 XRD of Al disks exposed to a 0.01 M Borax solution for 24 h at 55 and 85 °C

sample held at 85 °C is showing AlOOH peaks and must have a thicker film to be detected. Bunker et al. [11] reports that AlOOH is the only film grown initially at higher water temperatures, and it is the growth of this new film at 70 °C which is believed to cause the observed decrease in corrosion rate beginning at 70 °C in Fig. 6.

This slow down of Al corrosion with temperature can also be seen when measuring the amount of corrosion in loose powder in a beaker of water with time (Fig. 8). The increase in corrosion is dramatic moving between 55 and 70 °C; however above 70 °C the corrosion rate is higher for the first few hours, but then slows more quickly and after 6 h shows less overall corrosion. This can be important not only for rate concerns, but also for water management in portable systems using Al-assisted water split reaction to generate hydrogen, as the formation of AlOOH consumes less water than $Al(OH)_3$.

When looking at ball milled powders the initial corrosion rate is orders of magnitude higher than that seen with unmilled powders and also increases with solution temperature. However in solution volumes large compared to the amount of aluminum being reacted, such that the temperature rise within the solution is minimal throughout the reaction Czech [9] reports similar XRD results for reaction by-products. At 55 °C only $Al(OH)_3$ is seen, at 100 °C only AlOOH is found, and at temperatures in between both hydroxides are observed. If micro-environments were being created within the deformed surface, then localized temperature increases should favor the formation of AlOOH even with bulk solution temperatures at 55 °C.

3.3 Effect of surface area

With temperature and pH alone looking unlikely to explain the observed rate increase, determining the effective surface area of the ball milled aluminum was investigated. It is obvious that changes in milling parameters and second particle additives can have a huge effect on the final

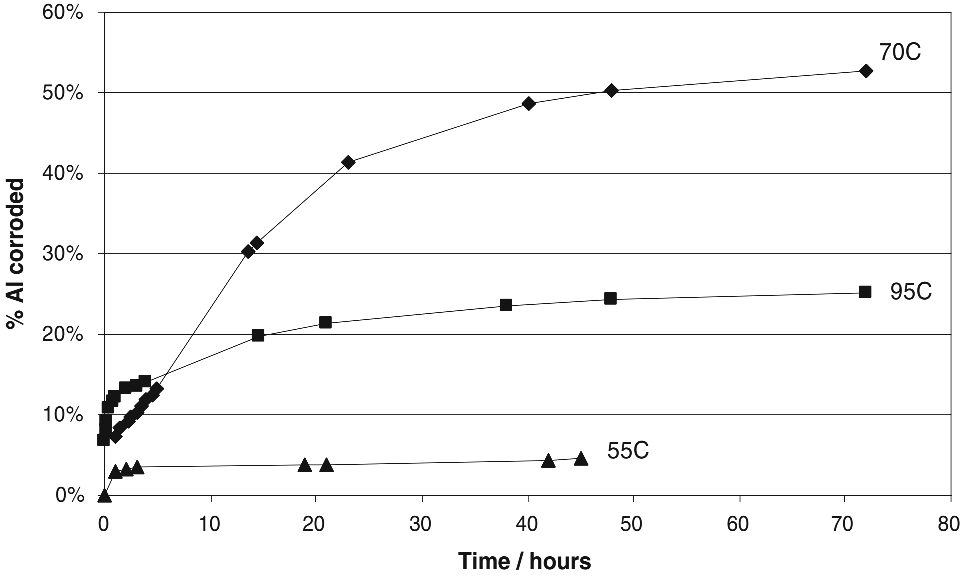


Fig. 8 Percent corrosion occurring with time for aluminum powder immersed in water at 55, 70, and 95 °C

surface area of the aluminum powder [9]. The difficulty was in determining the aluminum surface area from the total surface area of the ball milled mixture. Figure 9 shows the BET surface area for three ball milled mixtures of aluminum powder and alumina powder with the aluminum content ranging from 25% to 75%. These points form a straight line intersecting the surface area found for 100% alumina powder that had not been ball milled. This indicated that the oxide was not changing surface area as a result of the milling process and could therefore be subtracted out to give a value for the aluminum after milling.

Figure 9 can be interpreted two ways, first the aluminum has a similar surface area after milling given by the y intercept at roughly 1.5 m^2/g for all mixtures and the remaining surface area is the result of the alumina powder, or second, it can be assumed that the aluminum evenly coats the oxide and the measured surface area reflects the aluminum surface area. Distinguishing between these two possibilities can be done by comparing the corrosion rates for a given mass of aluminum with corrosion rates for a given surface area (Figs. 10, 11). Also helpful is to have a value for a 100% aluminum sample of high known surface area, for this a process used by Czech [9] of washed aluminum was used. In this method, aluminum powder is ball milled with a soluble salt (KCl), after milling the powder is mixed with cold water to dissolve the salt with little corrosion of the aluminum because of the low temperature. A series of washes is performed with the water being poured off and replaced each time, and then the remaining aluminum is slowly dried. This yields an aluminum powder that is >97% pure, with a surface area of over 13.5 m^2/g.

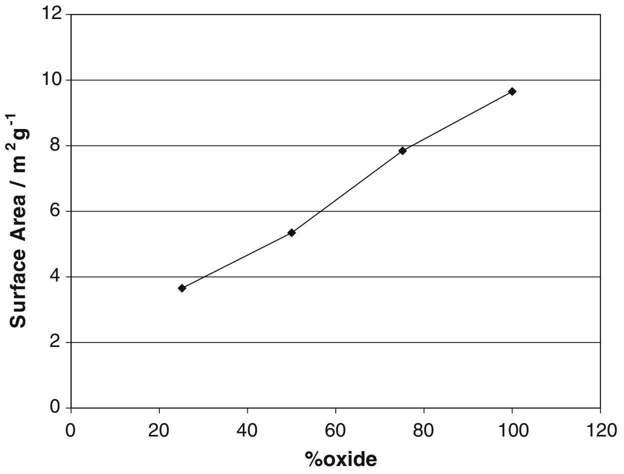


Fig. 9 Surface area of ball milled Al + Al_2O_3 mixtures varying the Al/oxide ratio

Figure 10 shows the corrosion rate for samples with the same amount of aluminum (0.5 g) milled with different amounts of Al_2O_3. This rate is determined by measuring the evolved hydrogen from each sample with time. The amount of hydrogen can then be divided by the theoretical value that would be seen if 100% of the aluminum was corroded. If the surface area after milling is similar between the samples then the corrosion rate should be similar as well, but instead the more oxide used the higher the resulting corrosion rate. At 75% oxide the aluminum is corroding at a rate similar to the 100% washed Al sample. Clearly the amount of oxide present is affecting the corrosion rate in a positive way, the second interpretation is that the greater amount of oxide allows for the aluminum to spread out over a greater area.

Figure 11 shows the equivalent rate of hydrogen evolution if all of the samples are normalized to have the same

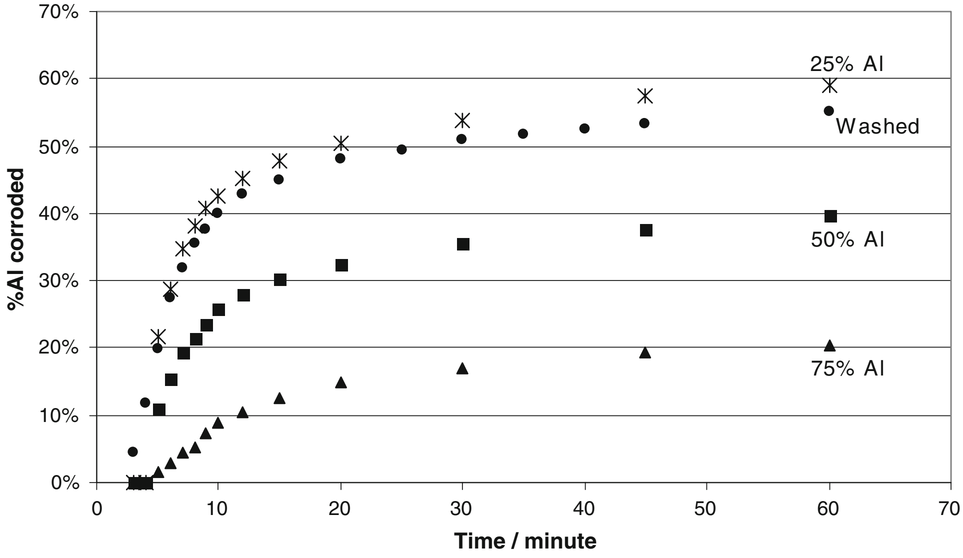


Fig. 10 The percent of aluminum that has corroded with time immersed in 70 °C water for BM powders with all volumes normalized to 0.5 g of Al. 25%, 50%, and 75% is the mass fraction of aluminum that has been milled with Al_2O_3, the "Washed" sample was Al milled 50/50 with KCl, with the salt subsequently removed from the sample leaving 100% Al

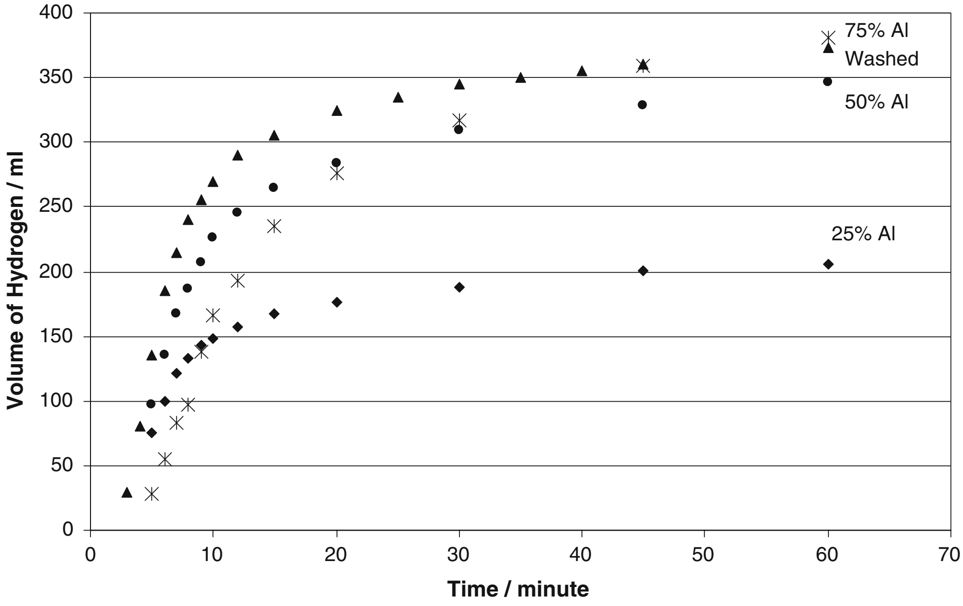


Fig. 11 The volume of hydrogen produced from aluminum that has corroded with time immersed in 70 °C water for BM powders with all volumes normalized to 6.8 m^2 of surface area. 25%, 50%, and 75% is the mass fraction of aluminum that has been milled with Al_2O_3, the "Washed" sample was Al milled 50/50 with KCl, with the salt subsequently removed from the sample leaving 100% Al

surface area as the 100% washed aluminum sample. In this case it is assumed that the area measured by BET for each mixture represents the actual aluminum surface area, with aluminum effectively covering the underlying oxide. Both the 50% and 75% sample have approximately the same hydrogen evolution rate as the 100% washed Al sample. The 25% Al sample is showing a decreased evolution rate compared to all the other samples and it is believed that there was insufficient aluminum to completely cover the oxide in this case and therefore the measured surface area by BET was also that of alumina. This resulted in a lower aluminum surface area than measured with the corresponding loss of rate. As the amount of oxide present increased there is a corresponding increase in time before hydrogen evolution began because of the greater mass of powder added that must be heated to solution temperature.

4 Conclusions

The corrosion of aluminum in water will increase both the temperature and pH.

The pH shift seen is not sufficient to greatly influence the corrosion rate.

The reaction by-product switches from $Al(OH)_3$ to AlOOH at temperatures above 55 °C for both milled and un-milled aluminum powders.

The lack of AlOOH in ball milled powders reacted at 55 °C is counter indicative of the idea that micro environments are formed by milling that see a localized temperature or pH shift different from the bulk solution.

In un-milled aluminum powders the AlOOH hydroxide is more passivating and decreases the overall corrosion of the aluminum powders for immersion times above 6 h.

For the milling conditions used, the surface area of the alumina (Al_2O_3) particles remained unchanged.

Hydrogen evolution rates scaled proportionately with surface area of the ball milled powders.

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