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## Combustion of Activated Aluminum with Water

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Aluminum-water reactions could be used for hydrogen and power generation as well as for underwater and space propulsion. A major obstacle, however, is the presence of a highly protective oxide film on the aluminum surface, which inhibits the reaction with water. Nanoscale Al powders usually react faster, but they have problems such a large amount of oxide on the surface and a high cost. It would be attractive to produce activated micron-scale Al powders. On the other hand, in the United States, there is a growing surplus of aluminum scrap and waste, conversion of which into useful products is highly desired. We have recently proposed the fabrication of an activated Al powder from Al foil using high-energy ball milling with sodium chloride and investigated the reactions of this powder with water at temperatures 35–80°C. It was shown that the obtained micron-scale powder rapidly reacts with water and the kinetics of this reaction was studied. The present paper focuses on the use of this powder for combustion with water. The powder was mixed with water with or without a gelling agent (polyacrylamide). Combustion of these mixtures in argon environment was studied experimentally. In contrast with conventional micron-scale Al powders, self-sustained propagation of the combustion front was easily achieved. The combustion temperatures and the front velocities were measured and energy dispersive X-ray spectroscopy (EDS) was used to characterize the condensed products. The micron-scale Al powder, obtained from foil, provides the combustion front velocity that is close to that for 38-nm Al powder, while offering a significantly higher content of active aluminum.

### 1. Introduction

The reaction of aluminum with water could be used for hydrogen generation on demand in fuel cell power systems (Xiani et al., 2013). Also, combustion of aluminum/water mixtures is of interest for space propulsion (Ingenito and Bruno, 2004; Miller and Herr, 2004), underwater propulsion systems (Foote et al., 1996; Waters et al., 2013), and combined hydrogen and power generation (Franzoni et al., 2010, 2011; Mercati et al., 2012). A major obstacle in all these applications, however, is the presence of a highly protective oxide film on the aluminum surface. This film inhibits the reaction of aluminum with water. Nanoscale Al powders usually react faster, but they have problems such a large amount of oxide on the surface and a high cost. It would be attractive to produce activated micron-scale Al powders. The known methods for activation of Al involve corrosion in strong alkaline solutions and alloying with bismuth, gallium and other dopants (Shkolnikov et al., 2011; Wang et al., 2009).

Recently, it has been reported that high-energy ball milling of Al powder with water-soluble inorganic salts such as sodium chloride produces an activated aluminum powder that readily reacts with hot water (Alinejad and Mahmoodi, 2009; Czech and Troczynski, 2010; Mahmoodi and Alinejad, 2010; Troczynski and Czech, 2008). Sodium chloride (NaCl) can be dissolved in cold water after milling and the remaining Al powder retains a high reactivity. As compared to other methods for Al-based water splitting, this process offers a number of advantages such as relatively low reaction temperatures (50–80°C), low cost of NaCl (which can also be recycled), and no need for rare, corrosive, toxic or environmentally harmful compounds.

We have proposed to increase the attractiveness of this method through the use of aluminum foil scrap and waste (Narayana Swamy and Shafirovich, 2012, 2013). The foil constitutes a large fraction of a growing surplus of Al scrap and waste in the United States. The conversion of this foil to useful products such as activated Al powders would have a positive impact on the environment. Also, the production costs of activated Al powders would significantly decrease as compared to using commercial Al powders as a precursor. We have shown that a highly activated Al powder can be produced directly from aluminum foil using high-energy ball milling with sodium chloride. This powder readily reacts with hot water, releasing hydrogen. Specifically, the reactions of the obtained powders with deionized water were studied over a temperature range of 35–80 °C. The induction period was longer for salt-free powders, apparently due to

aluminum oxidation during drying after washing in cold water. The effective activation energy of the reaction,  $63.1 \pm 3.1$  kJ/mol, determined using the temperature dependence of the maximum reaction rate, is in a good agreement with the data obtained previously for Al powders activated by ball milling with graphite (Streletskii et al., 2005). Milling in inert (argon) environment allowed a significant increase in the final reaction extent (up to 98% at the temperature of 80 °C).

In the present paper, we prepare mixtures of the obtained activated Al powder with water and study their combustion in inert gas environment. It is well known that mixtures of conventional micron-scale Al powders with water are not combustible, but the use of nanoscale powders allows preparation of combustible Al/H<sub>2</sub>O mixtures (Connell et al., 2011; Ivanov et al., 1994, 2000; Risha et al., 2007, 2008; Sabourin et al., 2008; Shafirovich et al., 2006, Sundaram et al., 2013). As noted above, however, nanoscale aluminum powders have a number of drawbacks. The use of activated micron-scale Al powders is a promising alternative to nano-aluminum in combustible mixtures with water.

## 2. Experimental Procedure

### 2.1 Fabrication of Activated Aluminum Powder from Foil

In most experiments, aluminum foil (ultra-pure, thickness 23 μm, VWR) was used as a starting material. The foil was cut into square (10 mm x 10 mm) pieces, mixed with sodium chloride (>99.0% purity, Sigma-Aldrich), and milled in a planetary ball mill (Fritsch Pulverisette 7 Premium Line), using 80-ml zirconia-coated grinding bowls and zirconia grinding balls (diameter: 2 mm, 5 mm, and 10 mm). The salt was preliminarily milled in the same mill in air environment for 10 min at 850 rpm using 10-mm grinding balls (the mass of NaCl was 5 g and the mass of balls was 44.7 g).

The Al foil pieces and the milled NaCl powder were milled together in either air or argon environment. In each milling process, 2 g of Al foil pieces and 2 g of NaCl were placed in the grinding bowl (the mill allows use of one or two bowls simultaneously). The milling process involved several cycles and the decrease in the diameter of grinding balls from 10 mm to 5 mm and then to 2 mm. The use of larger balls at the beginning allowed faster conversion of the foil to a powder, while the use of smaller balls at the end made this powder finer. The rotation speed was the maximum recommended by the manufacturer (Fritsch) for the specific ball size: 850 rpm for 10 mm, 1000 rpm for 5 mm, and 1100 rpm for 2 mm. The mass of grinding balls was 44.7 g for 10 mm and 44.5 g for 5 mm and 2 mm, i.e., the powder/balls mass ratio was about 1:11. Each milling step was followed by a cooling pause. Table 1 presents the ball sizes, rotation speeds, milling times, and cooling cycles in all cycles. The total milling time was 30 min. After completion of the milling procedure and final cooling, to break particle conglomerates, the powder was briefly (< 1 min) treated using a mortar and a pestle (both made of agate).

**Table 1. Parameters of the milling procedure.**

Cycle #	Ball diameter (mm)	Rotation speed (rpm)	Milling time (min)	Cooling time (min)
1	10	850	10	45
2	5	1000	10	60
3	2	1100	5	60
4	2	1100	5	

To remove NaCl, the obtained powders were washed in cold (< 15 °C) deionized water for 2 min. After passing the solution through a filter paper (about 20 min), the resulting Al powder was left overnight to dry.

The obtained powders were characterized using Brunauer-Emmet-Teller (BET) specific surface area analysis (Microtrac SAA), laser diffraction particle size analysis (Microtrac Bluewave), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS, Hitachi S-4800). The particle size analysis was conducted using isopropyl alcohol as a liquid carrier and ultrasonic treatment for deagglomeration.

## 2.2 Combustion of the Activated Aluminum Powder with Water

The obtained Al powder was mixed with deionized water in mass ratios of 1:1 and 1.5:1. The former ratio corresponds to the stoichiometry of the reaction:



which is expected to occur during combustion of Al/H<sub>2</sub>O system.

The mixture was placed in a quartz tube (O.D. 20 mm, I.D. 18 mm, length 50 mm), which was then installed inside a steel chamber (diameter: 30 cm, height: 40 cm), equipped with glass windows, a pressure gage, and feedthroughs for the ignition system and thermocouple measurements (Fig. 1). The chamber was evacuated and filled with ultra-high purity argon (99.999%). The mixture was ignited using a Nichrome wire heated by a DC power supply (Mastech HY3020E). Once the mixture ignited, the power supply was turned off. The combustion process was monitored using a video camera (Logitech Pro). Temperature inside the Al/water mixture during combustion was measured using a type C (W/5%Re – W/26%Re) thermocouple. The combustion experiments were conducted at pressure of 1 atm. Elemental composition of the reaction products was analyzed using EDS.

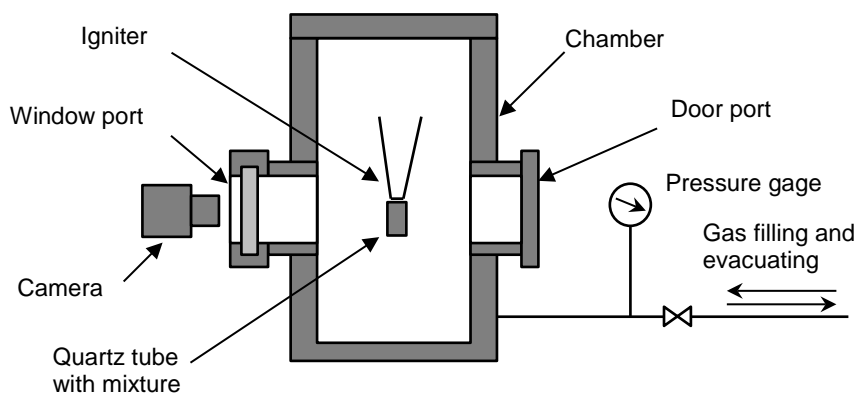
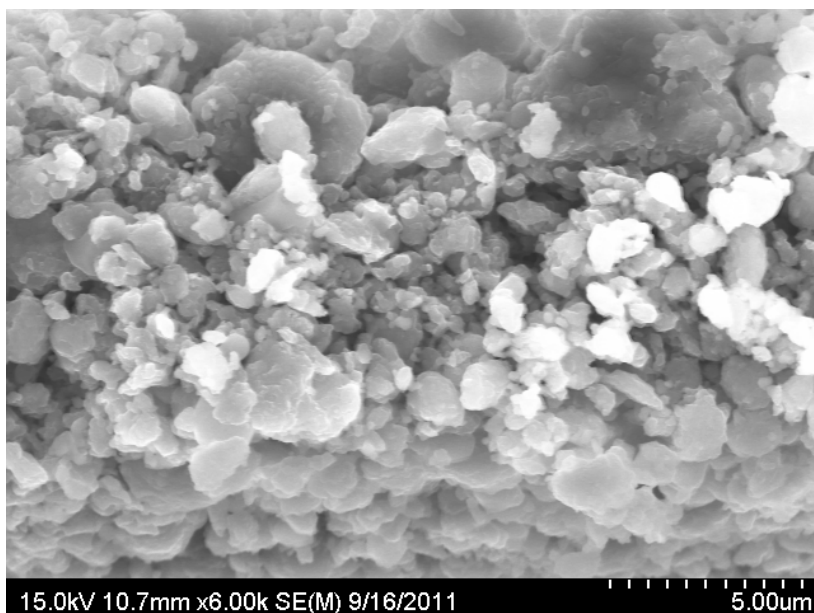


Fig. 1. Schematic diagram of the reaction chamber.

To observe the effect of addition of a gelling agent on the combustion characteristics of activated aluminum with water, polyacrylamide powder (nonionic water-soluble polymer, MW  $5 \times 10^6$ , Sigma Aldrich) was added to the Al/H<sub>2</sub>O mixture. Specifically, water and 3 wt% polyacrylamide were mixed until a gel was formed. Then the aluminum powder was mixed with the gelled water according to the stoichiometry of the reaction (Eq. 1). The resulting mixture was subjected to the same combustion procedure as described above.

## 3. Results and Discussion

Figure 2 shows the SEM microphotograph of a powder obtained by ball-milling of 23- $\mu\text{m}$  Al foil with NaCl. For this powder, the BET specific surface area is 4.7 m<sup>2</sup>/g, the mean volume particle size is 13.8  $\mu\text{m}$ , and the median diameter is 6.6  $\mu\text{m}$ . Thus, the employed high-energy ball milling produces a fine powder from Al foil mixed with NaCl. The decrease in particle size is significant owing to repeated fracturing of the particles, while the presence of salt in the mixture prevents cold welding of the particles.



**Fig. 2. SEM microphotograph of a powder obtained by ball-milling of 23- $\mu\text{m}$  Al foil with NaCl.**

Washing the obtained powder in cold deionized water for 2 min resulted in full dissolution of NaCl, which was confirmed by EDS (Table 2). The Al powder obtained after leaching out NaCl is finer than the original Al/NaCl powder: the BET specific surface area is  $10.6 \text{ m}^2/\text{g}$ , the mean volume particle size is  $8.5 \mu\text{m}$ , and the median diameter is  $5.0 \mu\text{m}$ .

**Table 2. Elemental composition of the obtained powders and the oxygen-to-aluminum atomic ratio.**

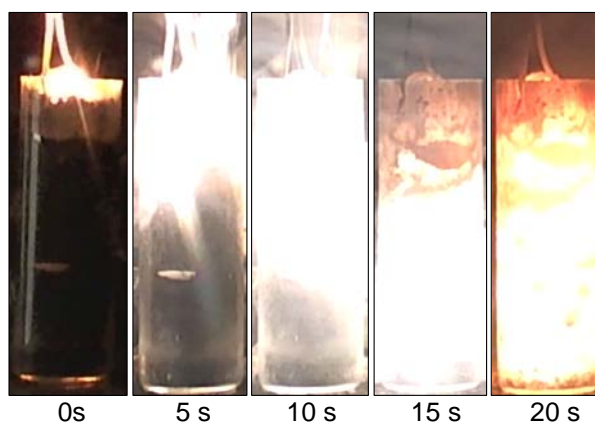
Milling Atmosphere	Wash time (min)	Elemental composition (at%)				O/Al (at%/at%)
		Al	O	Na	Cl	
Argon	0	43.07	2.99	26.47	27.22	0.069
Argon	2	86.23	13.77	0	0	0.159
Air	0	53.56	8.92	19.07	18.45	0.166
Air	2	82.88	17.12	0	0	0.207

Table 2 shows the powders obtained by milling in air contain larger amounts of oxygen. Apparently, for Al/NaCl powders, this oxygen is primarily a result of aluminum oxidation during milling, while the amounts of oxygen in the surface layer of the original foil are likely much smaller. For salt-free Al powders, the content of oxygen is somewhat higher independently on the milling atmosphere, which may be explained by additional oxidation of Al during drying after washing in cold water.

Self-sustained propagation of the combustion front was observed for combustion of mixtures of the obtained Al powder with water (Fig. 3). The entire combustion process from ignition to completion takes about 20 s. The combustion front velocities and the maximum temperatures recorded for the two mixtures (1:1 and 1.5:1) are shown in Table 3 (time 0 was chosen arbitrarily). It is interesting that with increasing Al content from 50 to 60 wt%, the maximum temperature decreases by  $300 \text{ }^\circ\text{C}$ , but the combustion front velocity increases two-fold.

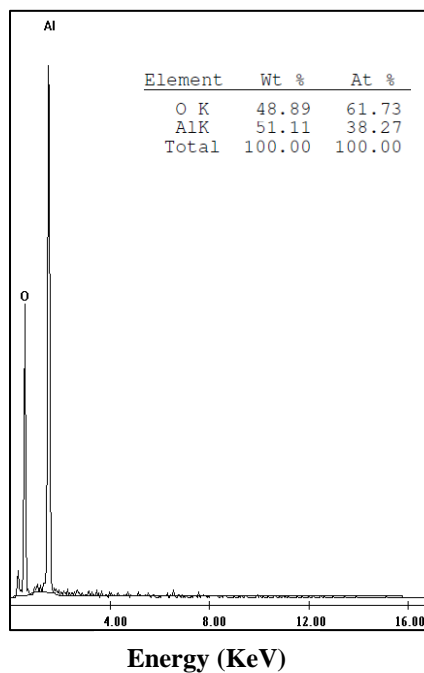
**Table 3. Combustion front velocities and maximum temperatures in experiments with different Al-H<sub>2</sub>O mass ratios.**

Al-H <sub>2</sub> O Mass Ratio	Combustion Front Velocity (mm/s)	Maximum Temperature (°C)
1 : 1	0.8	1752
1.5 : 1	2	1473



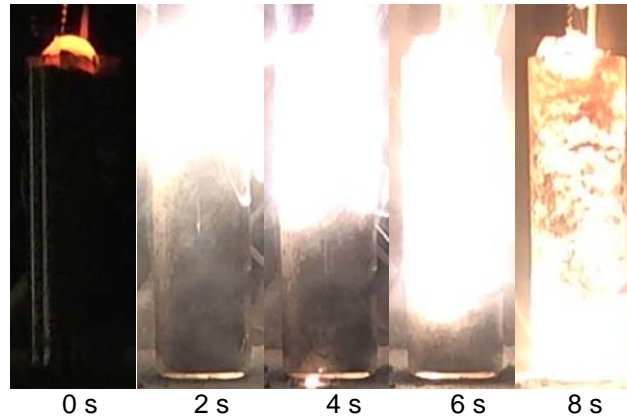
**Fig. 3. Combustion of Al powder with water at Al/H<sub>2</sub>O mass ratio of 1.5:1.**

The EDS spectrum for the reaction products of the combustion reaction of Al-H<sub>2</sub>O (stoichiometric ratio) is shown in Fig. 4. The obtained Al/O atomic ratio corresponds to Al<sub>2</sub>O<sub>3</sub>, which confirms that the reaction is described by Eq. 1.



**Fig. 4. EDS spectrum of products of Al – H<sub>2</sub>O combustion (Al:H<sub>2</sub>O = 1:1 by mass).**

Figure 5 shows combustion propagation over the mixture of the obtained Al powder with gelled water (3 wt% polyacrylamide) at Al/H<sub>2</sub>O mass ratio of 1:1. With the addition of polyacrylamide, the combustion front velocity increased from 0.8 mm/s to 6 mm/s.



**Fig. 5. Combustion of Al powder with gelled water (3 wt% polyacrylamide) at Al/H<sub>2</sub>O mass ratio of 1:1.**

Table 4 shows a comparison with data on the combustion front velocities in stoichiometric mixtures of nanoscale Al with gelled water at pressure of 1 atm. In all mixtures presented in Table 4, water was gellified by adding 3 wt% polyacrylamide. It is seen that the front velocity for the activated Al powder obtained from foil in the present work is significantly higher than for nanoscale Al powder with the size of 120 nm and close to the velocity reported for nanoscale Al powder with the size of 38 nm. Note that the 38-nm powder had an active aluminum content as low as 54.3 wt% (Risha et al., 2008). The micron-scale powder fabricated from foil has a much higher active Al content and hence offers significant benefits.

**Table 4. Combustion front velocities in stoichiometric mixtures of different Al powders with gelled water..**

Particle Size (µm)	Combustion Front Velocity (mm/s)	Reference
0.038	7	Risha et al. 2008
0.12	2	Ivanov et al., 2000
8.5	6	Present Work

Note that conventional, commercially available micron-scale Al powders do not form combustible mixtures with water and their addition to nanoscale Al/water mixtures dramatically decreases the combustion rate (Sundaram et al., 2013).

#### 4. Conclusions

An activated aluminum powder has been fabricated from aluminum foil by high-energy ball milling with sodium chloride, followed by washing in cold water for removing NaCl.

This powder was mixed with water and combustion of the obtained mixtures was studied in argon environment at 1 atm. With the addition of 3 wt% polyacrylamide to the water, the combustion front velocity significantly increased. The obtained micron-scale Al powder provides the combustion front velocity that is higher than for 120-nm Al powder and close to that for 38-nm Al powder, while offering a significantly higher content of active aluminum.

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