Synthesis of Bayerite-Passivated Aluminum Particles and Their Combustion in Solid Propellants

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then evaluated as a potential solid composite propellant fuel. Burn rate experiments were performed in a windowed pressure vessel, and condensed phase combustion products were recovered. Results show that the burn rate of hydrated μ Al (1.068 cm/s) is 17.75% higher compared to standard μ Al (0.907 cm/s) at 10.34 MPa with hydrated μ Al showing a clear particle suspension entrained near the burning surface. The hydrated shell enables oxidizing gas generation in proximity to the exposed Al core contributing to more complete combustion and accelerated burn rates at higher pressures. The solution-based hydration technique alters interface properties and affects the reaction mechanism and combustion demonstrated for propulsion applications.

KEYWORDS: aluminum surface hydration, alumina, bayerite, solid propellants, burn rates

INTRODUCTION

Aluminum particles are widely used in many energy generation applications because they store a tremendous amount of chemical potential energy (31 MJ/kg¹). The spherical particles are a shell–core structure because the metal core is naturally pyrophoric and requires passivation, or it will spontaneously combust when exposed to oxygen in the air. Synthesis of Al particles less than 25 μ m in diameter is based on atomization of bulk aluminum in a controlled environment.² As particles nucleate and solidify, oxygen is introduced to produce a 4–6 nm thermodynamically stable amorphous aluminum oxide (Al₂O₃) shell encapsulating the Al core.^{3,4} The passivation shell thickness is independent of the particle size.

greater than 96 wt % Al core retained. A detailed mechanism for surface hydration is discussed. The hydrated metal particles were

Aluminum combustion is based on mass diffusion between the metal core and an external oxidizer.^{5,6} Therefore, the Al₂O₃ shell is a barrier for aluminum oxidation reactions, and Al₂O₃ is a particularly good barrier. The melting temperature of Al₂O₃ is 2054 °C, and the molar enthalpy of fusion is $\Delta_{fus}H = 111.1 \text{ kJ/}$ mol.⁷ Also, as a paradox to the soft Al metal core, Al₂O₃ is one of the hardest ceramics with a hardness of 9 on the Mohs scale (compared to Al ~ 2).⁷ The nearly impenetrable properties of Al₂O₃ protect the Al core and retard diffusion reactions. Because power is the rate of energy release, Al particle oxidation produces far less power than monomolecular explosives. For example, assuming an equal mass (i.e., 1 kg), Al burns on the order of milliseconds⁸ compared to TNT on the order of microseconds.⁹ Power generated from Al oxidation is on the order of 31 kW, while for TNT it is 14,500 kW, despite Al having greater chemical potential energy (i.e., 31 MJ/kg compared to 14.5 MJ/ kg for TNT).^{1,10}

Increasing the power from Al particle combustion may be possible if alternative shell chemistries are considered. Researchers investigated ways to modify the nanoparticle shell using alternative coatings with favorable properties.^{11–14} One study showed that the terminal hydroxyl bonds on Al_2O_3 were instrumental in transforming a portion of the Al_2O_3 shell into an aluminum iodate hexahydrate iodic acid shell ([Al-

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 $(H_2O)]_6(HIO_3)_2(IO_3)_3$, called AIH).¹⁵ They showed with density functional theory calculations that the terminal OH bonds are weakest and most likely to promote the formation of the AIH. The new shell chemistry was formed by immersing Al particles into an iodic acid solution and enabling an acid—base surface precipitation reaction.¹⁶ The AIH-coated Al particles resulted in flame speeds on the order of 3200 m/s,¹⁷ exceptionally high compared to many thermite reactions.¹⁸ One explanation for the higher flame speeds was the abundance of the oxidizer in molecular scale proximity to an exposed core when AIH decomposed and dissociated.

Other researchers also used alumina surface hydroxyl bonds as a handle for chemical reactions involving carboxylic acids. Jouet et al.¹⁹ chemically formed self-assembled monolayers (SAMs) composed of fluorocarbons on the surface of nAl particles. The SAM-coated nAl particles dispersed in kerosene demonstrated exceptionally high combustion behaviors by reducing the onset of boiling by 50 °C and resulting in a 121% increase in initial burn rate constant compared to pure kerosene.²⁰ Crouse et al.²¹ applied various SAM coatings to nAl particles to enable nAl suspensions in liquid propellants, whereas uncoated nAl particles settle. The coatings enabled more complete combustion from the suspended nAl particles in liquid propellants, and all coatings used hydration bonds on the alumina surface to activate exchange reactions that produced the SAM.

Beyond nAl coating innovations, the surface hydroxyl bonds on alumina are active sites for catalysis reactions.^{22,23} Zhang et al.²⁴ studied core-shell Al-Al₂O₃ particles for propane dehydrogenation. Surface reactions produced hydrated alumina, specifically nanosheet-like structures of AlOOH and Al(OH)₃ formed on the particle surface. Their research showed that the hydrated alumina species were active sites promoting further reactions. However, Al(OH)₃ has more terminal hydroxyl groups than AlOOH²⁵ and therefore Al(OH)₃ is more favorable than AlOOH for promoting surface reactions. The idea of transforming the entire alumina shell into a hydrated derivative may provide an opportunity to enable new passivation strategies (rather than multilayer coating strategies) that lower the diffusion threshold barrier and more easily accelerate oxidation by supplying more oxidizers in the proximity of the exposed core aluminum.

One derivative of Al₂O₃ has been well studied in the context of chemical weathering. Specifically, the effect of heating and aging on Al_2O_3 particles in aqueous solutions to produce $Al(OH)_3$ has been an ongoing topic for research. There is an abundance of alumina in oceanic environments and understanding the degradation of its structural integrity due to corrosive saltwater environments motivates research. Abi Aad et al., Carrier et al., Lefèvre et al., Okada et al., and Cesteros et al. successfully hydrated Al₂O₃ particles using aqueous solutions by controlling parameters including solution pH and temperature, and time in solution (i.e., ranging from about 2 h to 4 months).²⁶⁻³⁰ Based on results from these studies, Malek et al.³¹ showed that the alumina shell of aluminum nanoparticles (nAl) powders can be successfully converted into Al(OH)₃ by pH modification in an aqueous environment. Her results showed that there are controllable aqueous conditions that will limit hydration reactions to the surface of the nAl. Limiting hydration reactions to the particle surface is important because hydrating the Al core sacrifices otherwise available chemical potential energy within the fuel powder.

Nanoparticles are not always preferred in energy generation applications, specifically for solid propellants. The active Al concentration in nAl is lower than μ Al particles (i.e., 75 wt % compared with 99 wt %, respectively) because the native alumina shell thickness is independent of particle size. The inherently higher concentration of alumina in nanoparticles adds an unusable weight that is undesirable for propulsion applications. Also, the activation energy for nAl is low compared to μ Al particles (i.e., 62 kJ/mol vs 130 kJ/mol, respectively, at 870–930 K⁵) such that nAl particles can be ignition-sensitive and require added safety precautions.^{5,32} Low active aluminum concentration and safety concerns associated with nanoparticles create a preference for μ Al particles in many applications.

The framework for designing a test matrix for surface hydration considering temperature and time in solution has been established from studies on chemical weathering of alumina.^{26–30} The objectives of this study are to identify the conditions required to hydrate the passivation shell of μ Al particles into Al(OH)₃, identify the hydration reaction mechanisms associated with surface hydration, and examine the combustion behavior of hydrated aluminum particles in a composite fuel propellant.

MATERIALS AND METHODS

Aluminum Surface Hydration

The Al powder was supplied from Valimet (Stockton, CA), product number H2. The particles have an average diameter of 2 μ m and a standard deviation of 1 μ m. A powder X-ray diffraction (XRD) pattern shows Al (PDF #04–007–9967) with 100% purity. Figure 1a shows a



Figure 1. SEM image (a) shows the particles are primarily spherical, and the TEM image (b) shows the alumina shell covering the Al core with shell thickness indicated.

scanning electron microscope (SEM) image of the spherical particles, and a transmission electron microscope (TEM) image (see Figure 1b) shows the particle core–shell structure with the shell 4–5 nm thick. The nascent oxide shell is composed of amorphous Al_2O_3 .

Hydrating the surface of μ Al particles was done by mixing the aluminum powder in a water solution for a prolonged period (Figure 2).



Figure 2. Sample preparation process for surface hydration of μ Al powder by controlling the temperature for a prolonged period.

Samples were prepared by mixing 230 mg of μ Al powder with 35 mL of deionized water. The solution was placed on a hot plate at 35 °C and continuously stirred by a magnetic stirrer at 350 rpm. Approximately 30 mg of powder was reclaimed starting from 17 h, then an additional 30 mg samples were collected at varied times over the next 10 h and placed in a fume hood to dry at ambient temperature. For scaling up the yield, the most important criteria are that the water-to-solid ratio should be such that all the powder is always in aqueous suspension for the duration of the aging period under heating.

Material Characterization

The standard and hydrated μ Al powders and postcombustion residue powders were analyzed using multiple techniques. Powder XRD analysis was performed with a Rigaku Miniflex II powder diffractometer using Bragg–Brentano geometry and CuK α radiation with a wavelength of 1.54059 Å at 30 kV and 30 mA. A step size of 0.02° scanned from 3 to 70° 2 θ , and the collection time was set from 0.1 to 0.6°/min depending on the samples. The peak intensity, position, and width of the diffraction patterns were processed using the whole pattern fitting Rietveld refinement method. The composition was identified using the MDI Jade V8.5 software and ICDD PDF 4+ database.

TEM and SEM were used to analyze the topography and morphology of the starting material and hydrated particles. Detailed descriptions of the TEM and SEM equipment are in Malek et al.³¹ The particle size distributions for the standard and hydrated Al were calculated by measuring particles in SEM images using *ImageJ* software. Approximately 125 particles were measured in each of three different regions of the powder sample, and the average diameter with standard deviation was reported.

The standard and hydrated μ Al powders were further analyzed by thermogravimetric analysis (TG). A NETZSCH Jupiter simultaneous thermal analyzer (STA) 449 F3 was used for this purpose. About 8 mg of powder was placed in an alumina crucible with a lid. A central hole in the lid enabled gas release during thermal equilibrium testing. The environment was 100% argon gas, and the samples were heated from 30 to 460 °C at a 10 °C/min heating rate. The NETZSCH Proteus software was used to analyze the data.

Propellant Formulation and Combustion

Propellants were prepared using 15 wt % standard μ Al or hydrated μ Al powder added to 70 wt % ammonium perchlorate (AP) powder with a 4:1 coarse to fine ratio (200 μ m:20 μ m) and 15 wt % binder. The composition for the binder is 10.8 wt % R45 hydroxyl-terminated polybutadiene, 2.3 wt % isodecyl pelargonate, and 1.9 wt % modified diisocyanate (MDI). The AP was passed through a size 70 mesh or 635 mesh sieve for coarse or fine particles, respectively, before incorporation. Each composite was hand-mixed for 1 h to promote mixture homogeneity. Following mixing, the propellant slurry was packed into a 2.5 × 7.5 × 0.63 cm mold and compressed with clamps until excess material was removed through overflow holes. The mold was placed in an oven at 55 °C for 1 week to cure.

After removal of the cured propellant from the mold, the propellant was cut into 6 mm \times 6 mm \times 25 mm rectangular strands. The 25-mm length was inhibited with a thin coat of nail polish to prevent unwanted burning on the sides of the strand. A 30-gauge Nichrome resistive wire was adhered to the top of the strand with a roughly 1:1 by weight mixture of coarse AP and nitrocellulose lacquer to ensure ignition.

Burn rate experiments were performed in a custom windowed pressure vessel schematically shown in Figure 3. Experiments were performed under nitrogen at elevated pressures of 2.1, 4.1, 6.9, 10.3, and 13.8 MPa, and three tests were performed per pressure. The propellant strands were imaged with high-speed videography (Vision Research, Phantom VEO) at 1000 fps with a 105 mm lens. Analysis of the video was used to measure the burn rates as a function of pressure and fit the data to empirical burn rate parameters of St. Robert's law.³³

The surface of the reacting propellant strands was imaged with a high-speed video camera (Vision Research, Inc. Phantom v2012) and a long-distance microscopic optic (Infinity Photo-Optical K2 lens) with a CF2 objective lens at 28,000 frames/s. The surface of all propellant samples was illuminated by two continuous 100 W white LED modules (Stratus LEDs).



Figure 3. Schematic of the high-pressure strand burner for the burn rate investigation.

Additional tests were designed to capture the solid residue postpropellant combustion. For these tests, the propellant strands prepared by using the standard or hydrated μ Al powders were placed in a test tube inside a sealed combustion chamber. The chamber held an air environment at atmospheric pressure, with exhaust ventilation to capture and scrub gases generated from propellant combustion. A similar ignition setup using a resistive hot wire and starter mix ignited the strand. The solid residue remained in the test tube postcombustion and was recovered for XRD analysis.

RESULTS AND DISCUSSION

The formation of Al(OH)₃ from Al₂O₃ in an aqueous suspension depends on the rate of surface dissociation of Al₂O₃.²⁶ Chemical weathering describes the process in which water molecules weaken the mechanical properties of the Al₂O₃ surface. Chemical weathering initiates the Al₂O₃ dissolution process and consequently the nucleation of Al(OH)₃ begins on the surface.^{34,35} When Al(OH)₃ particles grow, heterogeneous precipitation can occur. Abi Aad et al.,²⁶ Carrier et al.,²⁷ and Lefevre et al.²⁸ discuss that the formation of Al(OH)₃ from Al₂O₃ is highly dependent on solution temperature and time in solution. The Al(OH)₃ synthesis reaction from Al₂O₃ is given in eq 1, with Gibbs free energy (*G*) indicating a spontaneous reaction.²⁸

$$Al_2O_{3(s)} + 3H_2O_{(l)} \rightarrow 2Al(OH)_{3(s)}$$

 $\Delta G_{1atm,298K} = -24. \ 1 \text{ kJ/mol}$ (1)

The hydrolysis reaction in eq 1 is relatively slow under standard conditions (i.e., several days). The chemical bonds in Al_2O_3 consist of strong ionic bonds between cations (Al^{3+}) and anions (O^{2-}) as well as some covalent bonds in oxygen atoms. The ionic bonds hold strong electrostatic attractions that require a high energy to break. Consequently, the hydrolysis reaction in eq 1 without external heat, change in pH, or in the absence of an appropriate catalyst will be slow. Because of the relatively slow kinetics, the aging period for hydration of Al_2O_3 can take up to 7 days.^{26,27,29,30} However, over that relatively long duration of time (7 days), hydration reactions may extend into the core of the particle.

If hydration is not limited to the alumina shell but also permeates into the Al core, the Al core will react and form $Al(OH)_3$ and H_2 gas (see eq 2).

$$\begin{split} & 2\text{Al}_{(s)} + 6\text{H}_2\text{O}_{(aq)} \rightarrow 2\text{Al}(\text{OH})_{3(s)} + 3\text{H}_{2(g)} \\ & \Delta G_{1\text{atm},298\text{K}} = -887.\ 7\ \text{kJ/mol} \end{split}$$





Figure 4. (a) XRD patterns of μ Al particles hydrated at 35 °C as a function of time. (b) Magnified XRD plot of hydrated μ Al collected at 35 °C and 18 h. (•) Al(OH)₃: PDF No. 98–000–0111, (□) Al: PDF No. 04–016–2981. (c) TEM image of the same hydrated sample indicating a fuzzy surface texture. (d) *d*-spacings of the hydrated surface layer corresponding to Al(OH)₃.

The high Gibbs free energy of $-887.7 \text{ kJ/mol}^{36}$ indicates that eq 2 is more spontaneous than Al₂O₃ hydrolysis (eq 1). However, eq 2 is a redox reaction, and the standard reduction potential at 25 °C for Al is -1.676 V, and for water is -0.828 V.⁷ The small difference in standard reduction potential (i.e., -0.848 V) indicates a low driving force for electron transfer and therefore a relatively slow Al oxidation process in eq 2. Regardless, the aluminum and water reaction has been widely studied for the purpose of hydrogen gas generation.^{37–39}

The addition of heat accelerates both reactions (eqs 1 and 2) according to Le Chatelier's principle. However, at higher temperatures, the formation of AlOOH becomes favorable.^{40–42} To maximize oxygenated species in proximity to the Al core, Al(OH)₃ is more desirable than AlOOH. Therefore, relatively low heat balances the need to increase the hydration kinetics of eq 1 while limiting undesirable AlOOH formation.

The XRD patterns in Figure 4a show that a constant processing temperature of 35 °C and an aging period on the order of hours results in the formation of $Al(OH)_3$ on Al particles. Samples were collected starting from the 17th hour. The XRD patterns show $Al(OH)_3$ formation at 18 h (see Figure 4b). As the aging time increases, the $Al(OH)_3$ intensity increases, while the Al intensity decreases. The full-width half-

maximum (fwhm) intensity of the highest peak for $Al(OH)_3$ at 18.8 2θ and $\{hkl\} = \{001\}$ ranges from 0.098 to 0.214° 2θ , indicating narrow and sharp peaks corresponding to high crystallinity. The properly ordered crystal structure with high periodicity in the crystalline domain is consistent with well-formed $Al(OH)_3$ grains.

The TEM image of a hydrated particle (see Figure 4c) illustrates a fuzzy surface texture and *d*-spacings from image analysis (see Figure 4d) confirm Al(OH)₃. For five fringes, the lengths are measured at 1.35 nm (2.7 Å per spacing and {*hkl*} = {12–1}) and 2.07 nm (4.14 Å per spacing and {*hkl*} = {011}) which corresponds to Al(OH)₃ (PDF No. 98–000–0111). The phase of Al(OH)₃ detected in TEM is bayerite (β -Al(OH)₃). Bayerite was expected because the pH of the solution is 8, and previous work showed the phase of Al(OH)₃ nucleated at this pH was bayerite.^{43,44}

The gradually growing intensity of $Al(OH)_3$ with time is the result of an increasing $Al(OH)_3$ concentration. The weight percentages (wt %) of Al and $Al(OH)_3$ are provided in Table 1. The increasing concentration of $Al(OH)_3$ coincides with the declining concentration of Al as aging time increases, indicating hydration of the aluminum core and activation of both eqs 1 and2.

Table 1. Weight Percentages of Species at Indicated Aging Periods

time (h)	Al (%)	$Al(OH)_3$ (%)	impurity (%)
18	96.4	3.64	
22	37.5	59.4	3.1
26	2.1	90.5	7.4

Maintaining the aluminum concentration is important to ensure that maximum chemical potential energy remains within the particles after surface hydration. If the reaction stops earlier than 18 h, then the Al₂O₃ shell may remain. At 18 h, the shell is transformed into $Al(OH)_3$ with the least amount of core consumed. The spectroscopy data provide information on the extent of particle hydration. In Figure 5a, two points and one line are identified in the SEM image and analyzed for the chemical composition. For spectrum 1 in Figure 5b: the Al, oxygen (O), and carbon (C) wt % are 79.4:2.0:18.6, respectively. For spectrum 2 in Figure 5c, the Al, O, and C wt % are 70.8:8.7:20.5, respectively. Carbon is from the tape used on the sample holder. The line data are dependent on position; Al intensity increases at the core, whereas O intensity of the atom increases at the particle's edge (see Figure 5d). Figure 5d shows Al purity within the core, and the oxidizer surrounds the particle. The results in Figure 5d indicate that the hydration reactions occur from the surface of the particle and progress radially inward such that the core is not hydrated before the shell and remains intact after the interface hydrolysis reaction.

Samples were further investigated using EDS elemental mapping, and the aluminum core appears intact (see Figure 6). A thicker layer of $Al(OH)_3$ than the layer of Al_2O_3 in the standard material is observed. The density of $Al(OH)_3$ is less than Al_2O_3 (i.e., density of $Al(OH)_3$ is 2.42 g/cm³ compared to 3.97 g/cm³ for $Al_2O_3^{-7}$) such that the same mass of $Al(OH)_3$ consumes more volume than Al_2O_3 and makes the $Al(OH)_3$ shell appear thicker. From visual microscopy data, the $Al(OH)_3$



Figure 6. (a) SEM image and (b, c) EDS element mapping shows for hydrated particles Al is localized within the particle core while O surrounds the core. Thus, the particle processing parameters promote hydration reactions from the outer radius inward.

shell can range from 50 to 500 nm whereas the more condensed Al_2O_3 shell does not exceed 6 nm thick.

The particle size distributions of the standard Al and hydrated Al powder show a significant difference in average diameters (Figure 7). The neat Al particles have an average diameter of 2.05 μ m with a standard deviation of 1.00 μ m whereas the hydrated Al particles have an average diameter of 3.95 μ m with a standard deviation of 1.48 μ m. The change in the average particle size is caused by the distinct topography and lower density of the new Al(OH)₃ shell.

The TG analysis of the standard Al powder compared with the hydrated powder at 18 h is shown in Figure 8. For the standard Al powder, no change in mass is observed. The hydrated Al initially lost mass up to 141.6 $^{\circ}$ C due to the loss of physically



Figure 5. SEM-EDS data for the elemental composition of hydrated powders (a-c) indicating high wt % for Al and low wt % for O. The line data (d) for a single particle show the Al and O intensity is dependent on position with Al high within the core and O high at the particle surface.



Figure 7. Size distribution of μ Al particles shows that the average diameter of neat Al is 2.05 μ m and that of hydrated Al is 3.95 μ m. Approximately 125 particles were analyzed in both powders using microscopy images to evaluate size distribution.



Figure 8. TG and DTG as a function of temperature for hydrated powders processed at 35 $^{\circ}$ C for 18 h.

adsorbed water. Physically absorbed water is an artifact of bayerite's superhydrophilicity induced by the strong water-toaluminol hydrogen bonds in aqueous suspension⁴⁵ and can increase the weight by about 20%. This initial mass loss is followed by another mass loss up to 264.9 °C due to the dehydroxylation of $Al(OH)_3$. Equation 3 shows the dissociation reaction of $Al(OH)_3$.

$$2AI(OH)_{3(s)} \to AI_2O_{3(s)} + 3H_2O_{(g)}$$
(3)

The dehydration process leads to the formation of oxygen bridges between surface aluminum ions which increases the surface acidity at binding sites.⁴⁶ As a result, both mass losses in Figure 8 are followed by a slight mass gain as the newly activated surface readsorbs some oxide species.⁴⁷ The possibility of the particles oxidizing beyond oxygen from dissociated water is low because the TGA environment was 100% argon gas.

Figure 9 shows representative still frame images of burning propellants at atmospheric pressure containing standard μ Al (Figure 9a) and hydrated μ Al (Figure 9b) for comparison. The videos for these reactions are included in the Supporting Information. The hydrated μ Al propellant shows more particles popping and creating an apparent particle suspension seen as particles entrained in a gaseous cloud (Figure 9b) compared with the standard μ Al propellant (Figure 9a). The evaporation of physically adsorbed water and the release of vapor from dissociated $Al(OH)_3$ contribute to the more pronounced appearance of a particle suspension in Figure 9b.

Comparing Figure 9a,b also reveals increased light emission intensity for hydrated Al compared to standard Al propellants (see the Supporting Information for movies). The increased intensity may be an artifact of more hydrogen gas generation, more metal oxidation due to the removal of the shell barrier, or different intermediate species that emit more strongly in visible wavelengths. Differences in the production of intermediate species suggest an altered reaction mechanism. Higher emission intensity is an indication of higher heat release.

Figure 9c shows that the increased burn rate associated with the hydrated μ Al propellant at elevated pressures is measurably higher than the standard Al propellant. At elevated pressures, the added gases generated from interfacial hydration are suppressed toward the surface, enhancing heat feedback to the propellant and increasing the burn rate.

Figure 9 also shows the two propellants follow a similar trend for burn rate pre-exponential factor 'a' (0.32 for hydrated μ Al compared to 0.33 for standard μ Al) but show higher magnitudes for burn rate pressure exponent 'n' for hydrated μ Al propellant (0.51) compared to 0.45 for standard μ Al. The higher burn rate pressure exponent 'n' implies that hydrated μ Al has a higher sensitivity to changes in pressure than standard μ Al, which is influenced by the generation of more gas.

Table 2 shows the burn rates of propellants containing hydrated and standard μ Al. For 4.1 to 13.8 MPa, the burn rate ranges from 4.04 to 17.75% higher for hydrated μ Al than standard μ Al, consistent with Figure 9c.

The residue collected from three propellant combustion tests for standard and hydrated μ Al propellants were analyzed using XRD and results are shown in Figure 10. Table 3 summarizes the semiquantitative compositions including standard deviations. Table 3 shows standard μ Al propellant contains 15.97 wt % Al, and the rest is γ -Al₂O₃ (84.03 wt %), a metastable alumina phase. The postcombustion residue for the propellant with hydrated μ Al has only 9.9 wt % Al, 13.37 wt % α -Al₂O₃ (a stable alumina phase), 31.97 wt % γ -Al₂O₃, and the rest are other metastable alumina phases of θ and δ Al₂O₃ (see Table 3). The propellant with hydrated μ Al showed 6.07 wt % more Al reacted, implying that the hydrated shell induced more complete combustion than the alumina shell. The abundance of accessible oxygenated species in proximity to the Al core provided by the $Al(OH)_3$ shell and the relatively low energy threshold required to dissociate those oxygenated species (Figure 8) promote more complete oxidation reactions, evidenced by a lower concentration of unreacted Al in the recovered product residue.

The postcombustion residue from hydrated μ Al propellants shows an abundance of metastable alumina phases. The distinct variations in alumina phases detected in the product residue may be an indication of altered reaction mechanisms for the two Al powders. For example, Tran et al.⁴⁸ studied the combustion of similar Valimet H2 μ Al powders suspended in a porous polycarbohydrate matrix. They altered the standard H2 μ Al powder by applying an annealing and quenching treatment that reduced the surface energy of the particle and increased the particle dilatational strain. The altered properties were predicted to also alter the reaction mechanism. They recovered residue postcombustion and found a measurable increase in metastable alumina concentration for the annealed and quenched μ Al particles and attributed the distinction to an altered reaction mechanism. In another study, Chen et al.⁴⁹ used trifluoroacetic acid to corrode the surface of 3 μ m average diameter Al particles.



Figure 9. Surface imaging of burning propellants containing (a) standard μ Al and (b) hydrated μ Al. Images from videos provided in the Supporting Information are captured for atmospheric pressure conditions and show that more particles are popping away from the surface for the hydrated μ Al propellant. (c) Burn rate and burn rate pressure exponent '*n*' of hydrated μ Al are greater than standard μ Al. The pre-exponential factor '*a*' is similar for both propellants. Curve fitting: $R^2 = 0.9996$ for hydrated μ Al composites and $R^2 = 0.9825$ for standard μ Al composites.

Table 2. Burn Rates of Propellants Containing Hydrated μ Al and Standard μ Al

	standard μ Al		hydrated μ Al		
pressure (MPa)	burn rate (cm/s)	standard deviation (cm/s)	burn rate (cm/s)	standard deviation (cm/s)	
2.1	0.483	0.0119	0.483	0.0156	
4.1	0.629	0.0272	0.655	0.0263	
6.9	0.795	0.0127	0.831	0.0179	
10.3	0.907	0.0473	1.068	0.0387	
13.8	1.127	0.0424	1.230	0.1116	

Corrosion induced high surface porosity and altered the reaction mechanism relative to that of the pristine particles. The results shown in Figure 10 also suggest that interfacial reactions with bayerite in place of alumina may induce an altered reaction mechanism evidenced by distinctly more metastable phases of alumina.

CONCLUDING REMARKS

This study introduced a nontraditional method of modifying the alumina passivation shell surrounding an aluminum (Al) particle by inciting interfacial hydration reactions. Techniques derived from chemical weathering studies were applied to transform the $4-6 \text{ nm Al}_2\text{O}_3$ shell surrounding a crystalline Al microparticle into an Al(OH)₃ shell. Slightly heating the Al powder–water



Figure 10. XRD of the burnt residues from hydrated and standard μ Al propellants. The collected residue from standard μ Al contains Al [(\Box) PDF No. 98–000–0062)] and γ -Al₂O₃ [(Δ) PDF No. 98–000–0059] while the residue from hydrated Al contains Al, γ -Al₂O₃, α -Al₂O₃ [PDF No. 01–073–1512] and other phases of Al₂O₃ [θ -Al₂O₃: PDF No. 00–035–0121 and δ -Al₂O₃: 00–056–1186, both represented by (\bigcirc)].

solution to 35 °C for 18 h produced $Al(OH)_3$ on the surface, while 96% of the Al core remained intact.

The surface hydrated particles were tested for their burning characteristics at elevated pressures in propellants composed of

	Al	γ -Al ₂ O ₃	θ -Al ₂ O ₃	α -Al ₂ O ₃	δ -Al ₂ O ₃
hydrated Al propellant wt % (σ)	9.9(2.59)	31.97(13.37)	37.33(17.73)	13.37(3.75)	7.47(2.31)
standard Al propellant wt % (σ)	15.97(1.07)	84.03 (1.07)			

aluminum fuel, ammonium perchlorate, and binder. The results showed that the burn rates for hydrated μ Al propellants were higher than those for standard Al propellants at elevated pressures. Video data revealed the distinct appearance of entrained particle suspensions near the propellant burning surface influenced by more gas generation from dissociation of hydrated species from the surface Al(OH)₃. The apparent particle suspensions also promote a 12.5% higher burn rate pressure exponent, implying a greater sensitivity to change in pressure for hydrated μ Al propellants. Overall, the burn rate for hydrated μ Al propellant was up to 17.75% higher than that of standard μ Al propellant at elevated pressures. Postcombustion residue showed more unreacted aluminum (6.07%) in the standard μ Al propellant and a distinct difference in the formation of metastable alumina products, which is an indication of an altered reaction mechanism.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaenm.4c00161.

Standard Al propellant burn movie under atmospheric pressure conditions (MP4)

Hydrated Al propellant burn movie under atmospheric pressure conditions (MP4) $\,$

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Notes

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