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Surface modifications of plasma treated aluminum particles and direct evidence for altered reactivity

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Helium or argon plasma treatment of aluminum particles reduced the aluminum oxide shell by 40 wt%.
 Reduced oxide shells resulted in
- increased aluminum oxidation rates by an order of magnitude.
- Argon plasma treatment promoted particle surface hydration by 50 wt% while helium did not.
- Differences in Penning Ionization may contribute to metastable alumina formation and hydration seen in powders exposed to argon plasmas.

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ABSTRACT

Aluminum particles (Al) inherently contain a natural oxide (Al₂O₃) coating that limits rates of diffusioncontrolled energy release and can prevent complete conversion of the chemical energy available within an Al particle. Therefore, altering Al surface properties to reduce the oxide shell and/or transform shell chemistry are active areas of research. This study used atmospheric pressure plasmas to reduce the aluminum oxide shell, then examined the resulting changes in reactivity. Two plasma gas discharges were compared: argon (Ar) and helium (He). All plasma-treated particles were characterized using Powder Xray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA). Results show Ar plasma treatment resulted in high concentrations of surface hydration, while He plasma treatment did not. Both plasma-treated Al particles show reduced oxidation barriers that result in increased reaction rate constants by an order of magnitude for oxidation reactions. The results further an understanding of the effects of surface modifications on reaction kinetics and energy release behavior of fuel particles.

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1. Introduction

One challenge in our society is the advancement of energy generating materials that will power a wide range of mobile technologies. Inorganic materials, such as aluminum (Al) powder, are good

* Corresponding author. E-mail address: michelle.pantoya@ttu.edu (M.L. Pantoya). candidates and aluminum (Al) is accessible, inexpensive, and safe to handle. The high exothermic heat of combustion (i.e., 30.96 kJ/g or 400.5 kcal/mol) [1] for Al oxidation also makes Al appealing for localized energy generation [2,3] including applications such as welding and joining [4]. Unlike micrometer diameter Al particles (μ Al) that often experience incomplete combustion and are difficult to ignite, nanometer diameter Al particles (nAl) with a high surface area to volume ratio reduce diffusion distances and



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promote more interface contact facilitating diffusion-controlled oxidation [5,6].

The structure of an Al particle consists of a crystalline Al core and an amorphous oxide shell that includes two layers as depicted in Fig. 1: a loosely structured hydrated alumina (Al₂O₃) outer layer and a strongly bonded oxygen terminated Al₂O₃ layer at the interface of the Al core [7]. The Al₂O₃ passivation shell can be 4–6 nm thick regardless of particle size, such that nAl particles can have as little as 40 wt% active Al content while μ Al particles can have 99 wt% active Al content [8].

The multi-layer structure of the alumina shell has a strong influence on surface chemistry and modifications that promote combustion. For example, terminal OH bonds are active sites for surface reactions with halogenated species, such as fluorine [9,10] and facilitate Al fluorination reactions as described by McCollum et al. [2] and Ren et al. [3]. Also, the Al₂O₃ thickness is a diffusion barrier for oxidation reactions. Therefore, reducing the Al₂O₃ thickness should correspondingly increase mass diffusion rates for core oxidation reactions [11].

The application of atmospheric pressure plasmas is an emerging technique for processing powders, and specifically energetic materials. Plasma applications typically fall into two categories: (1) plasma-enhanced chemical vapor deposition (PECVD) or (2) plasma-enhanced surface treatments [11-18]. Abadjieva et al. [12], deposited fluorocarbon polymer coatings on micro-silica particles via PECVD to produce powders with improved processability and blast performance. Another study by Urbonavicius et al. [14] used low-temperature plasmas to modify the passivation of Al particles and promote hydrogen production in thermodynamically favorable aluminum-water reactions. Flannery et al. [16] developed an approach to passivate bare Al particles with a PECVD coating to improve powder de-agglomeration in aircraft fuels. Many of these plasma-based studies share a commonality: they are weakly ionized plasmas that utilize a dielectric barrier discharge (DBD) configuration in the generation of the atmospheric pressure plasmas. But, using a DBD to alter the surface of aluminum particles in order to influence their reactivity is a new approach for optimizing fuel powders for energy generation applications. Particle reactivity is a strong function of the oxide barrier naturally passivating the aluminum core such that variations in the passivation microstructure induced by plasma treatments will likewise affect particle reactivity and power generation.

The objectives of this study were to apply atmospheric pressure plasmas generated using a DBD configuration to reduce the thickness of the alumina shell on aluminum particles and assess variations in oxidation behavior resulting from the surface treatment. The nAl particles were characterized using X-ray diffraction (XRD) and thermal analysis including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The objectives were accomplished by designing thermal analysis experiments that compared untreated nAl powder to nAl powder that was plasma-treated using argon (Ar) or helium (He) plasma gas discharges for powder exposure times of either 10- or 30- minutes. The duration of exposure was predicted to have an influence on extent of surface modification of the particles. However, results showed negligible variations in surface features and reactivity with duration of plasma exposure albeit both plasma treatments increased the diffusion oxidation rate of the particles by an order of magnitude relative to untreated Al powder.

2. Experimental

2.1. Plasma treatment

The untreated (UT) commercial nano-aluminum (nAl) powder was supplied by Novacentrix (Austin, TX) and identified as UTnAl with a supplier specified 80:20 mass ratio of $Al:Al_2O_3$. The nAl powder used for all experiments contained spherical particles with a 80 nm mean diameter and the Al core was surrounded by an amorphous aluminum oxide shell that was 4–6 nm thick.

The nAl powders were plasma-treated with a lab-scale experimental setup shown in Fig. 2. The reactor consists of a 2.54 cm diameter by 20.32 cm long glass test tube wrapped in copper tape that was grounded, with a copper rod inserted in the center connected to a pulsed AC high voltage (HV) source. The copper rod was also shielded by another tube: an open-ended quartz tube with a thickness of 1.5 mm to maintain a dielectric barrier with a discharge gap of 5.3 mm. The input plasma conditions were maintained at peak voltages between 7 and 9 kV, 20–25 W load power, and 25 kHz pulse frequency.

Approximately 150 mg of UT-nAl powder was placed in the base of the plasma reactor before inserting the high voltage (HV) electrode and situating the gas inlet over the powder sample. A 10-min purge process proceeded each experiment using either



Fig. 1. Schematic of the Al particle core-shell structure with inset representing the native oxide shell with outer layer of physically adsorbed hydration. Note that Al atoms are blue spheres, oxygen are orange spheres, and hydrogen are yellow spheres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. A. Schematic of the DBD atmospheric plasma reactor setup. The inset shows a schematic of the UT-nAl (grey spheres) interacting with the plasma species: orange spheres represent He or Ar neutral gas atoms, blue spheres represent atoms that have lost an electron and become positively charged, and the free electrons are shown in red. B. Cross-sectional view of the DBD reactor. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

argon (Ar) or helium (He) at 1 standard liter per min (SLPM) flow rate. The purpose of the purge gas was to suspend the powder media and to mitigate exposure of atmospheric air in the reactor. The plasma treatments were conducted using either Ar or He also at a flow rate of 1 SLPM for a duration of either 10- or 30-min. Plasmas generated by Ar and He emitted a purple glow. Occasional arcing occurred from the lower part of the HV rod that was not fully enclosed, but arcing did not appear to interfere with the suspended powders within the purple glow of the DBD generated plasma.

At the conclusion of each plasma treatment, the particles were immediately suspended in acetonitrile (ACN) to arrest oxidation and identified as: plasma treated (PT) nano-aluminum (nAl), PTnAl. The particles were dried after suspension in a fume hood for a 24-h duration prior to material characterization.

2.2. Material characterization

Powder X-ray diffraction (XRD) data were collected on a Rigaku Ultima III powder diffractometer operating in continuous θ -2 θ mode from 15°-70° 2 θ with parallel beam geometry. Powders were mounted on a zero-background holder. The step size was 0.02° with a collection rate of 1°/min. The X-ray source was Cu K α radiation (λ = 1.5418 Å) with a current of 15 mA and an anode voltage of 30 kV. Diffraction intensities were captured with a D/teX Ultra 1D silicon strip detector. Data were analyzed using whole pattern fitting Rietveld refinement with MDI Jade V9.1.1 software to produce both a qualitative and quantitative analysis of crystalline species for all powder samples.

Differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) were conducted using a NETZSCH STA 449 F3 Jupiter simultaneous thermal analyzer (STA). Powder was kept between 5 and 10 mg and the powder sample was loaded in lidded alumina crucibles that were not hermetically sealed. A small pin hole in the lid of the crucible allows gas to flow out in order to quantify mass loss. Therefore, the only oxygen in contact with the powder sample was from the ambient air environment enclosed within the crucible. As a conservative estimate, for a 10 mg powder sample size, the concentration of oxygen held within the volume of the crucible was on the order of 2×10^5 ppm. All experiments were performed at a heating rate of 10 °C/ min with a flow of argon around the lidded crucible. For the thermal analyses performed here, equilibrium temperatures ranged from 30 to 800 °C. All data were processed with NETZSCH Proteus software to determine onset temperature and enthalpy for fluctuations in heat flow or mass change.

Transmission electron microscopy (TEM) was performed using a Hitachi H-9500 high resolution microscope operated at an accelerating voltage of 300 kV. Powder samples were prepared on TEM grids using the same ACN solvent used in the plasma treatment process. Image analysis was performed to reveal variations in morphology resulting from plasma interactions with powders.

Attenuated total reference - Fourier transform infrared (ATR-FTIR) spectroscopy analysis was carried out on a Vertex 70 FTIR spectrometer with a Platinum ATR accessory (Bruker Optics). The ATR measurement technique was used to identify surface hydration for the strongly absorbing powder samples. The FTIR was equipped with a MIR KBr beamsplitter and a room temperature MIR DLaTGS detector. Absorbance spectra were computed from 512 scans captured at 8 cm⁻¹ resolution.

3. Results and discussion

3.1. Plasma-treated nAl

There are two observed effects from the plasma treatment of nAl. The first is a reduction of the native oxide shell thickness and the second is the transformation from the original amorphous alumina structure to metastable phases of alumina and hydrated aluminum oxide. Both are described in more detail below.

The plasma treatment using either Ar or He gas result in visibly altered surface morphology and reduced aluminum oxide thickness to 2.7 nm, as previously shown in [19,20]. The reduction in shell thickness is regardless of the plasma duration or gas used to generate the plasma. When compared to UT-nAl, the oxide thickness was reduced by >40% [19,20]. The reduced Al₂O₃ thickness has been attributed to the flow of plasma gases affecting the weakly bonded exposed surface layer of the amorphous alumina shell (see Fig. 1) [7] and also localized electric fields within the plasma that etch the surface layer [18].

Fig. 3A shows the XRD patterns of the PT-nAl particles and distinct differences between the Ar and He plasma treatments. Specifically, the Ar PT-nAl particles are hydrated as boehmite, AlO(OH), and He PT-nAl particles show no hydration. In Supplementary Information, the Rietveld refinement data files (Fig. S1 and S2) indicate the hydration levels are >50 wt% for Ar PT-nAl. While the intensity appears low, Rietveld refinement is a whole pattern fitting technique that includes consideration of physical properties

Fig. 3. A. Full XRD pattern of all PT-nAl powders with crystalline species (i.e., Al and AlO(OH)) labeled. B. Zoomed-in region between 30 and 60° showing hydration peaks and indications of metastable alumina (specifically γ - and δ -alumina). Standards patterns of α - and γ -alumina are included (PDF 01-075-1863 and 01-079-1558) with experimental pattern of δ -alumina (PDF 00-004-0877).

and their interactions with X-rays. The analyses indicate 30-min Ar PT-nAl has 59.5 wt% AlO(OH) (Fig. S1) whereas the 10-min Ar PT-nAl has 56.3 wt% AlO(OH) (Fig. S2).

The metastable phases of alumina include γ , δ , θ -Al₂O₃ and under certain conditions these phases will transform to lower energy states of alumina until the transformation into α -Al₂O₃, which is the most stable phase and ground state. Looking closely at the XRD patterns in Fig. 3B, there are two minor peaks at 34° and 59° that correspond with metastable phases of alumina (γ and δ -alumina) [21,22]. Minor peaks between 36 and 37° are also associated with γ - and δ -alumina. In addition, the wide hydration peak between 45 and 50° indicates formation of boehmite. Fig. 4 shows ATR-FTIR spectra that were analyzed for Ar PT-nAl to provide further evidence of surface hydration. The broad spectra are characteristic of the stretching of —OH groups from adsorbed surface hydration on the Al₂O₃ shell [23].

At an inherently higher energy state, defects in the molecular structure of metastable alumina attract moisture from the environment that bonds with the alumina surface. Therefore, metastable phases of alumina such as γ , δ , θ -Al₂O₃ are hygroscopic compared to the stable alumina phase: α -Al₂O₃ [24,25]. The mechanism for hydration associated with Ar plasma and not He plasma is not yet understood. It is hypothesized that the interaction of Ar⁺ ions with the Al particle shell promotes phase transformations that result in metastable phases of Al₂O₃ that are hygroscopic whereas He⁺ ions promote formation of a more stable Al₂O₃ shell phase. However, the XRD patterns in Fig. 3B show no indication of stable,

 α -Al₂O₃ in any sample. The metastable alumina phases shown in Fig. 3 measurably decrease in intensity from He to Ar treatments. The decreased intensity may be an indication that the metastable phases inherent in Ar-PT-nAl transformed into AlO(OH) thereby reducing peak intensity of metastable Al₂O₃. Hydration could be induced upon immersion in ACN (which is a polar solvent), or hydration may occur from the ambient surroundings once the powders were dried and stored. The samples were all stored in sealed containers and in an ambient environment for the same duration before testing.

The differences in surface hydration (Fig. 3) may be explained by a unique process called Penning Ionization (PI) that occurs between excited gas-phases and targeted molecules [26,27]. Penning ionization occurs when the ionization potential of the target molecule (M) is lower than the excitation energy of the ionized gas (G^*). When $M < G^*$ the reaction produces a neutral gas molecule (G), an electron (e^-), and a cation molecule (M^+) shown explicitly in Reaction (1) [27].

$$G^* + M \to M^+ + e^- + G \tag{1}$$

The He plasmas were demonstrated by Hiroaka et al. [27] to have sufficient energy to enable PI to occur, and therefore suggests potential for our He plasmas to produce similar energy, although not experimentally measured or modeled here. Since the outer surface of the alumina shell is weakly bonded and the shell thickness is reduced upon plasma treatment, the target molecule will be atomic oxygen in the Al_2O_3 structure rather than surface hydrox-

Fig. 4. ATR-FTIR spectra of Ar PT-nAl with broad spectral bands between 2600 and 3700 cm⁻¹ indicative of surface hydration.

yls. Both plasma reactors are purged such that no ambient oxygen is assumed to be present. Since the excitation potential of excited gas-phase Ar has been demonstrated to be lower than the ionization potential of oxygen [27,28], PI may not occur for Ar plasmas as it could in He plasmas. The process of PI may contribute to differences in alumina phase that lead to hydration differences between samples. Future work will require more characterization of the generated Ar and He plasmas.

TEM micrographs of He and Ar PT-nAl are shown in Fig. 5 and indicate spherical Al particles result after He plasma exposure (Fig. 5A) but in Fig. 5B, Ar PT-nAl particles appear highly fragmented with smaller sub-particles that may be hydrated species separate from the parent particle. In Wu et al. [29], following plasma treatment in the same DBD reactor configuration, portions of the oxide shell were transformed to γ -Al₂O₃. The chemically rich environment provided by plasma discharges [18] may be transforming part of the etched oxide shell on the Ar PT-nAl to an activated metastable alumina phase, such as γ -Al₂O₃ which is naturally hygroscopic [24,25], leading to the formation of the fragmented hydrated species. The observation that no hydration is present in He PT-nAl implies that the oxide shell is still stable following the He plasma exposure.

The TGA curves of mass change compare all plasma treatments (PT-nAl) to UT-nAl and are shown in Fig. 6 by the duration of plasma exposure (10- or 30-min) and gas discharge (He or Ar). The percent mass change is indicated as % gain (\uparrow) or loss (\downarrow) along

with dashed lines indicating onset temperature for mass change in Fig. 6A. A kinetic analysis of Ar and He PT-nAl is presented in Fig. 6B and C, respectively, and discussed below.

As shown in Fig. 3, Ar PT-nAl particles include boehmite (AlOOH) and significant mass loss is correspondingly observed in Fig. 6. Thermal dehydration studies of boehmite by Fitzgerald et al. [30] and Alex [31] shed light on the decomposition behavior of Ar PT-nAl particles. The initial mass loss occurring at temperatures below 100 °C is attributed to the removal of physically adsorbed surface water and is typically seen in poorly crystalline or "pseudo boehmite" materials [30]. The slightly higher onset temperature for dehydration (78 °C vs. 88 °C for 10- vs. 30-min Ar PT-nAl, respectively) implies that a longer exposure of the particles to the plasma creates a more structurally stable hydrated state with slightly delayed (i.e., by 10 °C) onset temperature for dehydration.

Fitzgerald et al. [30] conducted nuclear magnetic resonance (NMR) experiments that identified two important regions of dehydration that occur in AlO(OH) before transformation to γ -Al₂O₃: a lower temperature region (100–300 °C) where physically adsorbed water is removed and a higher temperature region (350–550 °C) where water molecules are removed by internal condensation of the water protons and Al-coordinated hydroxyl groups in the structure of "pseudo boehmite" material. The first and second stages of decomposition in Ar PT-nAl (Fig. 6) generally fall within the regions where the physically adsorbed surface water is

Fig. 5. A. TEM image of He PT-nAl with reduced oxide shells. B. TEM image of Ar PT-nAl showing fragmented damage to nAl core (yellow arrows) with sub particles that may be indicative of hydrated content. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. A. Mass changes labeled in terms of percentage of total sample mass. Note that the percentage with \uparrow represents percentage mass gain and \downarrow represents percentage mass loss. B. Kinetic analysis for calculating reaction rate constants, *k*, for Ar PT-nAl and UT-nAl with dashed lines representing the rate of reaction occurring in each stage of decomposition (Table 1). C. Kinetic analysis for calculating reaction rate constants, *k*, for He PT-nAl and UT-nA with dashed lines representing the rate of oxidation (Table 2).

removed and surface Al-OH groups begin to condense, as observed in Fitzgerald et al. [30] and Alex [31]. However, removal of Al-OH groups occurring at temperatures above 400 °C is likely overshadowed by oxidation reactions consuming the Al core and associated mass gain observed in the third stage (Fig. 6B). Mass loss stages are not observed in He PT-nAl (Fig. 6A) and there is no measurable presence of boehmite in He PT-nAl in Figs. 3, 4, and 6.

To better understand the kinetics of AlO(OH) decomposition on Ar PT-nAl particles, reaction rate constants were calculated from the TGA data shown in Fig. 6B using Eqs. (1)-(2) adapted from Fogler [32]. A power-law model for homogeneous reactions was postulated for the rate law assuming first-order reactions with the rate calculated by the integral method.

$$-\frac{dm}{dt} = km \tag{1}$$

$$\ln\frac{m}{m_0} = -kt \tag{2}$$

The initial mass of PT-nAl is m_o , m is the mass at time t, and k is the reaction rate constant. The positive and negative signs of k indicate mass loss or mass gain, respectively. The TG data were curve-fitted to calculate k values shown with dashed lines in Fig. 6B, and since all experiments were conducted at 10 °C/min in the same environment, k represents a rate constant within the indicated temperature range.

Table 1 distinguishes the two stages of decomposition and third stage of oxidation observed from Fig. 6B, with the reaction rate constant calculated for each stage and its corresponding mass loss or gain. In the first stage, mass loss is 16.4% and 17.8% for 10- and 30-min Ar PT-nAl, while UT-nAl does not undergo a mass change. In the second stage, mass loss is 6.0% and 7.8%, and no change is observed for UT-nAl. In the final stage for temperatures above 510 °C and 408 °C for 10- and 30-min Ar PT-nAl, overall mass gain is 2.3% and 0.5%, respectively. Overall, the first two stages of mass loss exhibit similar kinetics for both exposure times and correspond well with the removal of hydrated species described in

Table 1

Comparison of dehydration and oxidation rate constants for Ar PT-nAl with UT-nAl. Dehydration stages correspond with AlO(OH) dehydration stages described in [30,31].

Temperature range	k (min ⁻¹)	Mass loss \downarrow / gain \uparrow (%)	Description
78–247 °C	0.014	16.4 ↓	Removal of surface adsorbed water
247–510 °C	0.003	6.0↓	Removal Al-OH groups
> 510 °C	0.001	2.3 ↑	Oxidation
78–235 °C	0.016	17.8↓	Removal of surface adsorbed water
235–408 °C	0.006	7.8↓	Removal Al-OH groups
> 408 °C	0.0004	0.5 ↑	Oxidation
> 400 °C	0.0004	1.1 ↑	Oxidation
	Temperature range 78–247 °C 247–510 °C > 510 °C 78–235 °C 235–408 °C > 408 °C > 400 °C	Temperature range k (min ⁻¹) 78-247 °C 0.014 247-510 °C 0.003 > 510 °C 0.001 78-235 °C 0.016 235-408 °C 0.006 > 408 °C 0.0004 > 400 °C 0.0004	Temperature range k (min ⁻¹) Mass loss \downarrow / gain \uparrow (%) 78-247 °C 0.014 16.4 \downarrow 247-510 °C 0.003 6.0 \downarrow > 510 °C 0.001 2.3 \uparrow 78-235 °C 0.016 17.8 \downarrow 235-408 °C 0.006 7.8 \downarrow > 408 °C 0.0004 0.5 \uparrow > 400 °C 0.0004 1.1 \uparrow

Fitzgerald et al. [30] and Alex [31]. The third stage shows a net mass gain attributed to exposure of the dehydrated surface to surrounding oxygen and the ensuing exothermic oxidation that exceeds simultaneous endothermic dehydration reactions.

The difference in the onset temperature in the third oxidation stage (Table 1) between the 10- and 30-min Ar PT-nAl is likely due to an increased concentration of AlO(OH) in 30-min Ar PT-nAl sample. As previously mentioned, the 30-min Ar PT-nAl has 59.5 wt% AlO(OH) whereas the 10-min Ar PT-nAl has 56.3 wt% determined by Rietveld refinement (Fig. S1 and S2). In Alex [31], the onset of dehydration reactions in the 350–550 °C range were shifted to lower temperatures as the milling time of AlO(OH) powders increased due to an increase of imparted surface energy which caused a delay in the removal of adsorbed hydration. The delay in temperatures indicated an increased removal of hydroxyl ions when Al₂OH condenses to AlOH in the range of 100–350 °C. Simi-

 Table 2

 Comparison of reaction rate constants for He PT-nAl with UT-nAl.

Sample	k at T > 400 °C (min ⁻¹)	Mass gain (%)
10-min He	0.0016	8.3
30-min He	0.003	5.3
UT-nAl	0.0004	1.1

larly, the increased mass loss (17.8%, Fig. 5A) in addition to a higher rate constant (0.016 min⁻¹, Table 1) observed for 30-min Ar PT-nAl likely contribute to increased removal of hydroxyl ions in the second stage of Al-OH condensation. This is also a reasonable explanation for the decreased onset temperatures for the third oxidation stage by 112 °C for the 30-min Ar PT-nAl. For the third stage, the small rate constant for 30-min Ar PT-nAl may quantify competing dehydration and oxidation reactions and may not be representative of oxidation, especially because the lower onset temperature remains in the dehydration temperature range and the net mass gain is only 0.5%.

Fig. 6C shows mass gain behavior as a function of time for the He PT-nAl and UT-nAl particles with dashed line curve fits for rate constant calculations of oxidation. Steady mass gain is observed in He PT-nAl after 400 °C and 50 min, clearly indicating oxidation. Table 2 shows the rate constants are 0.0016 min⁻¹ and 0.003 min⁻¹ for 10-min and 30-min He PT-nAl, respectively which are one order of magnitude higher compared to the rate constant of UT-nAl (0.0004 min⁻¹). The higher rates of oxidation for He PT-nAl particles are consistent with the reduced oxide shell barrier resulting from plasma treatment. The reduced oxide barrier facilitates diffusion through the shell to oxidize the particle core at a higher rate. It is interesting to note that the shorter 10-min plasma exposure nearly doubles the oxidation rate relative to the sample with longer He plasma exposure. While the thickness of the shell was

Fig. 7. Heat flow curves from DSC scans of He PT-nAl, Ar PT-nAl, and UT-nAl in an oxygen deficient environment. Curves are shifted vertically for ease of comparison.

Table	3
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Summary of calculations for relative enthalpy based on measured values from Fig. 7.

Sample	Reaction of Al core and relative enthalpy				
	Onset (°C)	Peak (°C)	Percent Al Reacted Before Melting (%)	Percent Al Melting (%)	Melting Enthalpy (J/g)
30-min Ar	653.4	660.7	96.5	3.4	13.3
10-min Ar	654.3	662.3	91.9	8.1	31.53
10-min He	657.2	665.4	38.8	61.1	239.1
30-min He	657.8	665.9	36.1	63.8	250.0
UT-nAl	650.8	659.7	20.0	80.0	313.1

reduced equally for the two exposure durations, the cause for the differences in rate constants are not known and future work focused on He plasmas should analyze powder exposure duration more systematically.

Fig. 7 shows the heat flow curves from the DSC scans of all PTnAl compared to UT-nAl and includes the relative enthalpy of melting and estimated percentage of Al that melts. The melting enthalpy is relative to UT-nAl and for reference is 10.56 kJ/mol for Al [33].

Table 3 summarizes the data in Fig. 7 and includes the calculated percent of Al that contributed to the melting enthalpy. The melting enthalpy decreased significantly for Ar plasma treatments indicating core aluminum was consumed before the melting temperature. The Ar plasma treatment not only induced hydration, but hydration may have partially consumed the core Al. In the slow heating environment of the DSC, nearly all the aluminum from the core was consumed prior to melting by dehydration and also oxidation. The He PT-nAl did not exhibit hydration such that the plasma effectively thinned the oxide shell enough to accelerate oxidation and consume more of the core Al than UT-nAl. However, an appreciable amount of core Al remained because the melting enthalpy is roughly 60% of the Al available.

There are two main conclusions from Fig. 7 and Table 3. First, exposure of the nAl powders to Ar plasma high concentrations of hydrated species may form into the Al core. Since exothermic trends for Ar PT-nAl are not significant in Fig. 7, hydration is an explanation for reduced Al content measured via Al melting in Fig. 7. Second, the thinned oxide shell resulting from plasma treatment enhances early stages of oxidation seen especially in He-PT-nAl by the larger exothermic trend in Fig. 7 and evidenced by reduced Al core content relative to UT-nAl.

4. Conclusions

The surface of nAl was altered via atmospheric plasma surface treatments using Ar and He plasmas at exposure times of either 10- or 30-minutes. Plasma processing reduced the oxide shell thickness by 40%. Results do not differ by plasma exposure times. The XRD and TG data showed Ar PT-nAl particles were hydrated in the form of boehmite (AlO(OH)) while the He PT-nAl particles exhibited no hydration. Excessive hydration may be an artifact from the Ar generated plasmas, localized temperatures could have transformed the oxide shell to a metastable phase that is more hygroscopic and promoted hydration. Both the He and Ar plasma treated nAl particles were shown to oxidize in the DSC more readily than untreated-nAl. Results from plasma processing nAl particles demonstrate the potential of enhancing energetic performance by manipulating particle surface structure and inducing chemical transformations at the particle surface.

All of these results have implications for the use of plasma treated nAl particles for power generation applications. First, hydrated alumina surfaces may provide excellent platforms for altering the shell chemistry in ways that may transform energy release behaviors for nAl particle combustion. Hydrated alumina promotes surface reactions that typically include halogens and could enable the formation of new halogenated passivation shells that produce different reaction mechanisms and provide more rate-controlled release of chemical energy during aluminum combustion. Second, reduced thickness or hydrated alumina surfaces will be weaker passivation structures relative to untreated alumina passivation and may introduce alterations in ignition sensitivity to impact, friction, and/or electrostatic discharge. The safe handling of plasma treated nAl should be considered more thoroughly because while the reduced oxide shell may produce an order of magnitude higher diffusion oxidation rates, the reduced shell thickness or hydrated shell may also reduce the energy thresholds for ignition in ways that could influence handling.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Michelle Pantoya reports financial support was provided by US Army Research Office. Kelsea Miller reports financial support was provided by US Army Research Laboratory.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2021.110119.

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