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Brief Communications

Plasma surface treatment of aluminum nanoparticles for energetic material applications

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A R T I C L E I N F O

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ABSTRACT

Aluminum nanoparticles (nAl) have great potential for energetic applications. However, the native oxide shell (amorphous alumina, Al_2O_3) inhibits efficient energy release and acts as a barrier for aluminum (Al) oxidation. An energetic oxidizer, aluminum iodate hexahydrate (AIH), has recently been demonstrated as an effective coating for nAl. However, the current chemical synthesis method has led to widely varying AIH concentrations on nAl particles. Plasma surface treatment of nAl is a novel "energy coupled to material" technique which alters the nAl surface properties without changing the bulk active Al core. This work explores a new approach to engineering the nAl surface using atmospheric argon (Ar) plasma to accomplish two objectives: (1) reduce the nAl oxide shell thickness, and (2) synthesize AIH on the treated particle surface. Transmission electron microscopy (TEM) reveals more than 40% reduction in the oxide thickness after 10 min Ar plasma treatment. Laser-induced air shock from energetic materials (LASEM) experiments show significant energy release enhancements for the plasma-treated nAl with AIH coating (PT-nAl-AIH) compared to commercial nAl as well as untreated nAl with AIH coating (UT-nAl-AIH). The results demonstrate the potential of applying atmospheric plasma techniques to modify nAl for enhanced reactivity.

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1. Introduction

Aluminum nanoparticles (nAl) possess high surface area to volume ratio and stored chemical energy. The amorphous alumina (Al_2O_3) shell is an effective catalyst for surface exothermic chemical reactions [1]. However, releasing stored chemical energy within the particle via diffusion-controlled chemical reactions is limited due to the Al_2O_3 shell surrounding the crystalline Al core and acting as a barrier. The Al_2O_3 shell also reduces the mass ratio of active Al core as the Al particle size reduces. Therefore, control of the interfacial properties and mitigation of the oxide shell are crucial. Smith et al. [2] demonstrated the possible removal of the Al_2O_3 shell by using a highly acidic iodic solution (HIO₃) to reduce the amorphous shell outside the Al core and the resultant formation of the oxidizing salt, aluminum iodate hexahydrate (AIH), has led to enhanced reactivity. Nevertheless, the approach has also resulted in inconsistent AIH content and intense particle agglomerations.

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Utilizing plasmas to modify nAl is a new approach to improve nAl reactivity through changing the surface of nAl particles. The present work examines the hypothesis that nAl surfaces can be modified using argon (Ar) plasmas and those modifications can alter energy release during reaction. The plasma-treated nAl (PTnAl) particles are immersed in the iodic acid solution to alter the chemistry of the passivation shell and induce greater overall energetic performance, which is evaluated by a laboratory-scale energetic test technique called laser-induced air shock from energetic materials (LASEM).

2. Experimental

Fig. 1 shows the atmospheric dielectric barrier discharge (DBD) plasma reactor. The prototype design consists of a regular test tube (8" length, 1" inner diameter and $1\frac{1}{4}$ " outer diameter) wrapped in a copper tape acting as the ground electrode, and a copper electrode in the center, connected to high voltage and shielded by a dielectric (hollow quartz tube). The Ar gas enters the reactor through a gas line inserted into the reactor with the gas exit just above the nAl with a flow rate of one liter per minute. The plasma is generated by a nanosecond AC pulsed power source with \sim 4–6 kV,





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Fig. 1. Schematic (a) and a photo (b) of the DBD atmospheric plasma reactor setup.

25 kHz, and 20 W input conditions. The nAl powders (NovaCentrix Inc.) contain crystalline Al core and 4–6 nm thick amorphous Al_2O_3 shell, as shown in Fig. 2a. The nAl powders have a wide size distribution based on transmission electron microscopy (TEM) imaging

(60–100 nm), while the manufacturer specifies an 80 nm average diameter. Approximately 150 mg nAl is placed at the bottom of the reactor (Fig. 1) and first purged with Ar for 10 min, then placed in contact with plasma for 10 min. The plasma-treated nAl (PT-nAl) is then immediately suspended in either 1) acetonitrile (ACN) to prevent re-oxidation; or, 2) an iodic solution by hand-mixing for the formation of AIH, identified as PT-nAl-AIH – followed by air drying in a fume hood under ambient conditions. The equivalence ratio for initial mixing of the nAl: I_2O_5 : water is kept constant at 1:1:2.5 by mass.

The PT-nAl-AIH particles are characterized by TEM (JEOL 2100FX), powder x-ray diffraction (PXRD)(Rigaku Ultima III), and LASEM. All images presented are taken with a JEOL 2100FX microscope operated at a 200 keV accelerating voltage.

The LASEM procedure involves the pulsed laser (Nd:YAG, 850 mJ, 1064 nm, 6 ns) ablation of the sample resulting in approximately $100 \mu g$ of the material being ejected into the air above the sample surface, forming a high temperature plasma. Details of this method are reported elsewhere [3]. The laser-induced plasma produces a laser-induced shock wave; the expansion of the shock wave into the air is imaged by a high-speed camera and used to obtain a characteristic laser-induced shock velocity. A material that produces a faster laser-induced shock velocity is indicative of a material with a faster energy release rate.



Fig. 2. TEM BF images showing (a) the UT-nAl particles with several representative Al_2O_3 thickness specified by yellow arrows; (b) the PT-nAl particles showing a reduced oxide thickness after the plasma treatment; (c) the rough surface of a single PT-nAl particle; (d) the further reduced shell thickness of PT-nAl-AIH; (e) the highly non-uniformly distributed AIH particles on the PT-nAl-AIH sample as darker spots; (f) the elemental map of PT-nAl-AIH showing the sporadic AIH crystals on the particle surface.

3. Results and discussions

Fig. 2 shows images of nAl particles at different stages of processing, including Fig. 2a untreated nAl particles (UT-nAl), Fig. 2b and c plasma-treated nAl particles (PT-nAl), and Fig. 2d-f plasmatreated nAl-AIH particles (PT-nAl-AIH). Fig. 2f is an elemental map acquired corresponding to a high-angle annular dark field image with a 1 nm probe size. As clearly specified in Fig. 2a, the Al₂O₃ shell thickness is measured from approximately 4 to nearly 6 nm for as-received nAl particles. After Ar plasma treatment, the shell thickness is reduced to 2.7 nm in average (Fig. 2b), most likely due to the plasma-assisted breakdown. The reduced oxide shell thickness does not change the overall particle size significantly except for those relatively few extremely small nAl particles (<20 nm), and the reduced oxide shell thickness appears to remain the same after re-examination of the same sample after 6 months (not shown). However, we are aware of literature on changes in the amorphous alumina structure that result from annealing [4]. It is noted that hydrogen plasma-metal reaction (HPMR) method has been reported to form hydrogenated metallic nanoparticles via vacuum plasma techniques [5]. Unfortunately, addition of hydrogen into Ar plasma is not suitable for the atmospheric DBD plasma approach exploited for this work which has the advantage of experimental simplicity. In addition to the reduced Al₂O₃ shell, the PT-nAl surface also exhibits a rough morphology (Fig. 2c). Such altered surface roughness can contribute to increased surface contact between nAl and the iodic solution for the formation of AIH, leading to a greater overall reactivity. In these preliminary experiments, the shell has not been completely removed after plasma treatment.

Fig. 2d shows that PT-nAl-AIH particles not only exhibit a further reduced shell thickness to 1 nm, but also excellently preserves high crystallinity for the nAl core. The further reduced Al₂O₃ shell can be attributed to the dissolution of the thinner PT-nAl shell in the iodic solution to form AIH crystals through a polarization reaction mechanism [6]. Results from XRD analyses estimate 58 wt.% AIH content and reveal additional crystalline species including hydrogen iodate and beta iodate in PT-nAl-AIH (not shown). The TEM images also demonstrate the non-uniformity and highly sporadic distribution of AIH on PT-nAl-AIH particles, shown as the darker spots in Fig. 2e due to the higher mass nature of iodine. This can be attributed to both possible non-uniform plasma treatment on nAl due to the settling of nAl at the bottom of the reactor rather than uniformly dispersing in the plasma glow, and the hand-mixing of PT-nAl powders in iodic solution. The elemental map shown in Fig. 2f confirms the presence of iodine-containing species, most likely AIH crystals, sporadically accumulate and attach on the surface of PT-nAl-AIH particles. The map is consistent with the TEM image (Fig. 2e).

Fig. 3 shows the LASEM results at the microsecond timescale analogous to a detonation event. The bar in red is for PT-nAl-AIH from the current study. The green bars are UT-nAl-AIH (with 6 wt.% and 15 wt.% AIH) from Gottfried et al. [3], and the blue bars are individual components present in the formation of Al-AIH. The laser-induced shock velocity for PT-nAl-AIH is 26% faster than nAl and 7.8% faster than the 15 wt.% AIH-containing UT-nAl-AIH. A higher laser induced shock velocity for PT-nAl-AIH can be attributed to both the increase in AIH content (58%) and the reduced oxide shell. A mechanism for the higher energy release rate of PT-nAl-AIH may be explained by the chemical structure of AIH that contains a hydrate ring around Al^{3+} that separates the iodate species from Al^{3+} . Dehydration of the ring facilitates AIH decomposition to expose Al^{3+} and react at lower temperatures than the native Al_2O_3 shell [2].



Fig. 3. The laser-induced air shock velocities normalized to Al_2O_3 from the LASEM measurements at the microsecond timescale relevant to a detonation event.

4. Conclusion

This work presents a new exploration of Ar plasma surface treatment on aluminum nanoparticles (nAl) to reduce the inactive amorphous Al₂O₃ shell, leading to increased AIH concentration up to 58 wt% and enhanced reactivity. While the AIH coating is sporadic and not uniform, the AIH-containing Ar-plasma treated nAl sample (PT-nAl-AIH) still exhibits significantly enhanced reactivity based on laboratory-scale LASEM test results. The LASEM result for PT-nAl-AIH demonstrates a 7.8% greater reactivity at the microsecond time scale relevant to a detonation event than previously studied untreated nAl-AIH particles (UT-nAl-AIH) prepared without using plasma. The preliminary results clearly demonstrate the potential of using inert plasma treatments to alter the surface morphology and properties of nAl using Ar plasma as an example. However, in-depth materials characterizations are needed to elucidate possible interactions between the Al₂O₃ shell and different plasma gases.

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