Characterizing the coating and size-resolved oxidative stability of carbon-coated aluminum nanoparticles by single-particle mass-spectrometry

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Abstract

Aluminum nanoparticles are of significant interest in enhancing the rate of energy release from propellants. One of the major impediments to their use is that bare aluminum is highly reactive, while oxide coated aluminum significantly decreases overall performance. We investigate creating aluminum nanoparticles with a thin carbon coating using either a laser induced plasma or a DC plasma-arc. The carbon coating was created by injecting ethylene (C_2H_4) directly downstream of the plasma. The elemental composition of the coated aluminum nanoparticles was measured in real time with a recently developed quantitative single particle mass spectrometer (SPMS). We found that the aluminum nanoparticles were coated with a carbon layer of thickness around 1–3 nm.The thermal and oxidative stability of these particles was determined by passing the aerosols through a heated flow reactor in a carrier flow of either air or argon, and measuring the aluminum, carbon and oxygen content in the particles with the single particle mass spectrometer. We found that below 700°C the coating was stable, but that the coating oxidized above ~800°C. In contrast the carbon coating was thermally stable above ~900°C. These results indicate that a carbon coating may be a suitable passivating agent.

Introduction

Aluminum nanoparticles have attracted considerable interest as a possible fuel in advanced energetic material applications. Recently, several studies have been conducted to quantitatively answer; how reactive aluminum nanoparticles are (Aumann et al., 1995; Ivanov & Tepper, 1997; Park et al., 2005), and to understand the effect of size on reactivity (Park et al., 2005). Not surprisingly, it has been found that the reactivity of aluminum particles is greatly enhanced with

decreasing size, resulting from the increased surface area-to-volume ratio.

On the other hand, the decreased particle size can also lead to a number of undesirable effects, most particularly high reactivity at low temperatures, and the associated difficulty in handling the materials safely. The usual practice to reduce the reactivity at low temperatures is to passivate the surface with a thin oxide layer. However, as particle size decreases, particularly so at the nanoscale regime, the oxide layer represents a significant fraction of the mass of the particle,

which results in a decrease in the energy release per unit mass. For example, the oxide coating constitutes ∼36% of the mass of 20 nm aluminum particle with only 2 nm oxide coating. This leads one to investigate alternative passivating agents.

An ideal coating material for an energetic particle should be non-reactive at low temperatures, and oxidize or evaporate under elevated temperatures. To our knowledge, there has been only one attempt to passivate aluminum particles for energetic applications. Jouet et al. (2005) coated aluminum nanoparticles in solution using a perfluoroalkyl carboxylic acid self assembled monolayers (SAMs). They showed that the SAM coating passivated the aluminum and prevented the oxidation of the particles in air.

In this paper we study the properties of carbon as a passivating layer, by using either a laser ablation method, or a DC arc to create, and coat aluminum nanoparticles in a continuous manner. We will use single particle mass spectrometry to study size-resolved particle stability of these coated aluminum particles in heated air and argon, and compare with the corresponding uncoated particles.

Experimental

For the generation of coated or uncoated aluminum nanoparticles, we used both, a laser ablation and a DC arc discharge method. For laser ablation, a 1064 nm Q-switched Nd:YAG laser operating at 10 Hz with a pulse width of 4 ns was used to ablate a solid aluminum pellet (99.99% pure from Sigma–Aldrich Inc). The schematic of the laser ablation method is shown in Figure 1. The laser beam is focused through a fused silica plano-convex lens (focal length = 100 mm) to a spot on the solid aluminum target, with an approximate laser fluence of $\sim 10^{10}$ W/cm^2 at the focal point. This generates a local micro-plasma at the surface of aluminum target, leading to vaporization of aluminum. The aluminum target was mounted on a rotating shaft with an attached stepper motor, so that the target surface could be rotated with a
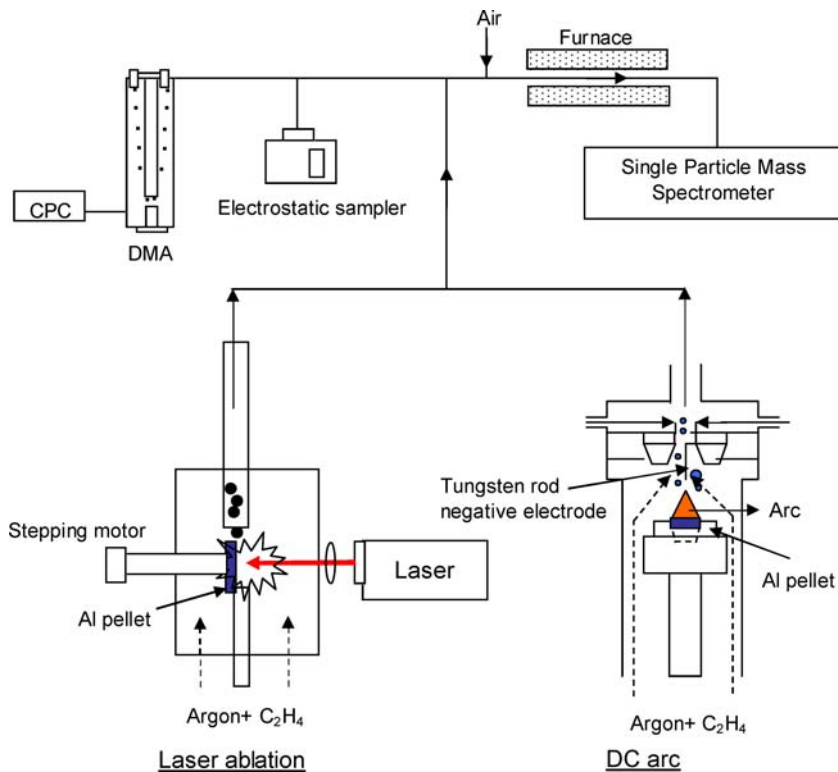

Figure 1. Schematic of the experimental system for particle generation and characterization.
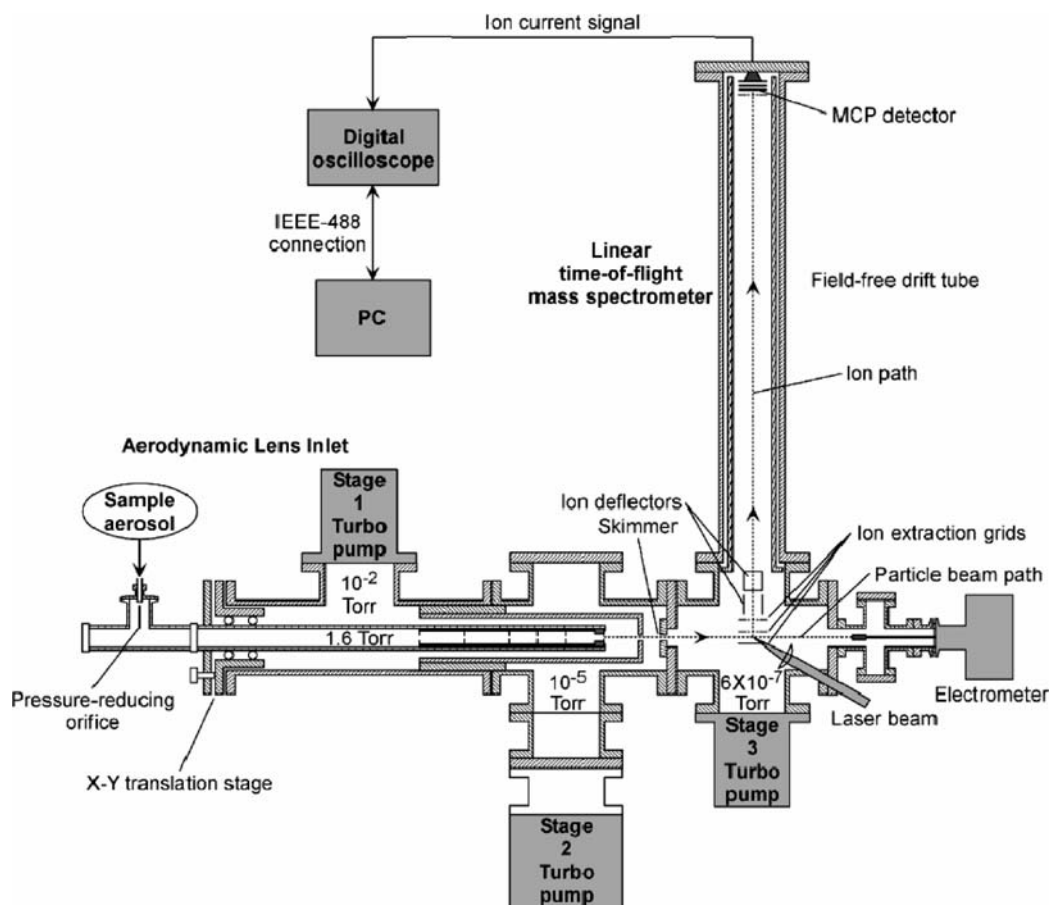
Figure 2. Schematic of Single Particle Mass Spectrometer.

controlled interval to provide long term stability in the particle generation process. A flow of argon was continuously swept past the target surface to carry away the aluminum vapor, and cause rapid quenching and nucleation of aluminum.

In the DC-arc discharge method as shown in Figure 1, an arc is ignited between a tungsten electrode and aluminum pellets, which serves as the heat source to evaporate aluminum. The negative electrode is a tungsten wire clamped between two carbon pieces. A carbon basket holding the same aluminum pellets as used in the laser ablation method serves as the anode. An infinite amperes arc welder is used as a DC power supply to the apparatus. A stable arc was achieved at 15–20 V, and currents of 25–50 A. Aluminum nanoparticles are subsequently created by an argon quench flow (22–30 LPM).

To produce coated aluminum nanoparticles, we added ethylene (C_2H_4) to the argon quench flow with an argon–ethylene volumetric flow ratio of 10 to 1, with the object of causing thermal cracking of the carbon precursor and heterogeneous nucleation at the particle surface.

The coated or uncoated aluminum nanoparticles produced in this way are introduced in real time to the single particle mass spectrometer (SPMS) (Mahadevan et al., 2002; Park et al., 2005) where their elemental composition and size can be determined. To measure the oxidation behavior of coated or uncoated aluminum nanoparticles, or to examine the thermal stability of the coated film, the aerosol flow mixed with air or aerosol flow itself is passed through a heated reactor tube at a constant temperature for a known residence time (~1 s), the output of which is sampled by the
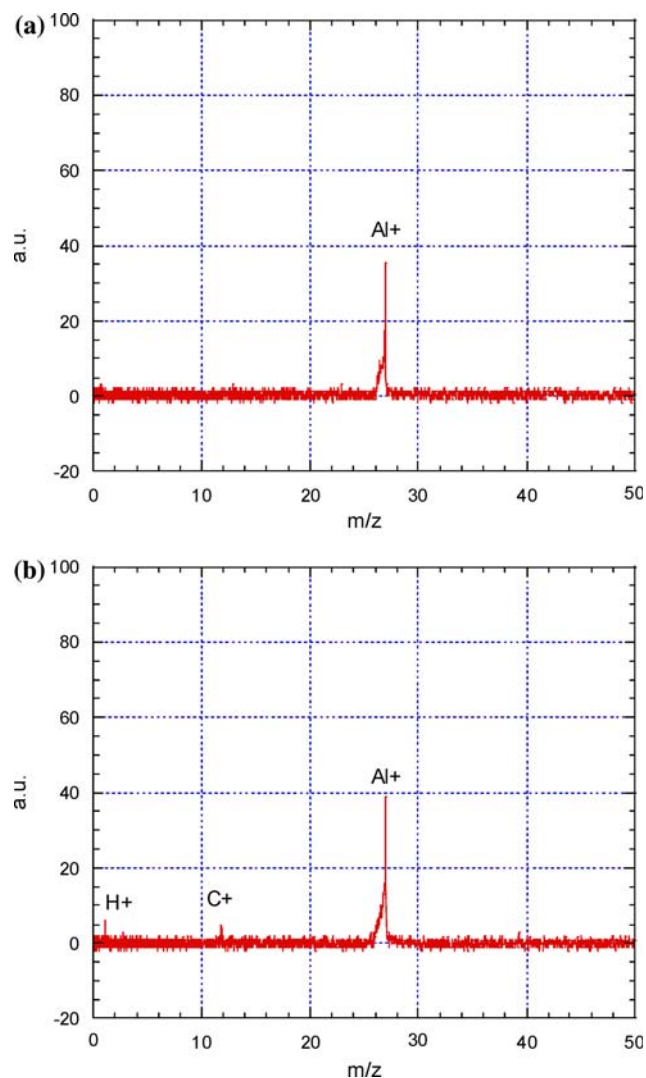
Figure 3. Typical single particle mass spectrum for bare aluminum nanoparticles (a) with a quench gas of argon and (b) carbon coated aluminum nanoparticles with argon and ethylene mixture (10:1).

SPMS. We can determine any change in elemental composition resulting from reaction with air or from heating for both the coated and uncoated case.

Detailed descriptions of the SPMS can be found in our previous papers (Mahadevan et al., 2002; Park et al., 2005). Briefly, the SPMS consists of an aerodynamic lens inlet, three stage differential vacuum system, a free firing pulsed laser for particle ionization, a linear time-of-flight mass spectrometer, and a 500 MHz digital oscilloscope and

PC for data acquisition, as shown in Figure 2. The aerodynamic lens system produces a narrow collimated particle beam, and transports particles in the range of 30–300 nm into the high vacuum system with high transmission efficiency (Liu et al., 1995). The 10 Hz free firing frequency double Nd:YAG pulsed laser (532 nm) is used as the ablation/ionization source. In order to ensure complete ionization, the beam is focused through a 2 cm spherical plano-convex lens, into the extraction field of the tof-mass spectrometer, and
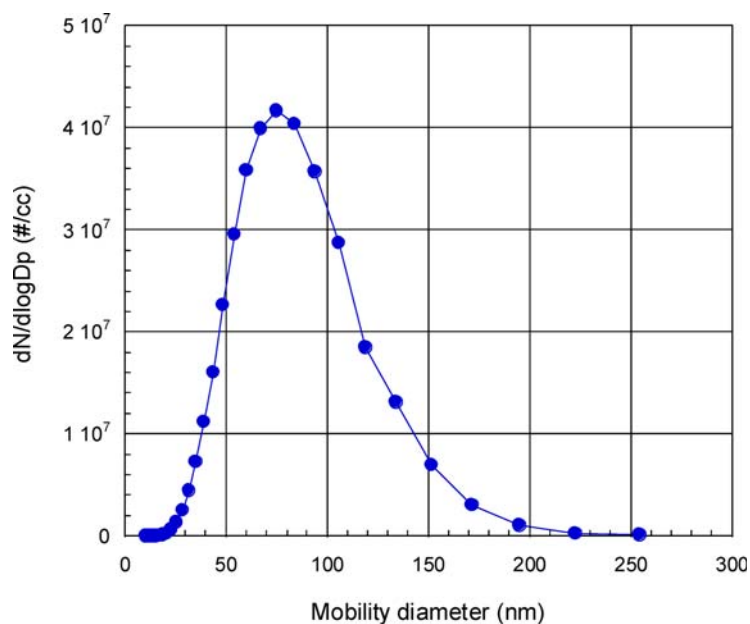
Figure 4. Size distribution measured with the DMA and CPC for coated aluminum particles produced from the laser ablation method.

intersects the particle beam at the focal point. We typically operated the laser with a pulse energy of ~100 mJ, which corresponds to a peak laser power density at the focal point of approximately ~10^{11} W/cm^2. When the laser hits a particle, positive ions formed from the particle travels along ~1 m time-of-flight tube, and are detected by microchannel plates (MCP) detector.

Because of the complete ionization approach being used here, the relative ion signals from different masses can be used to get the particle stoichiometry quantitatively, and the integrated mass signals can be summed to provide a measure of the total particle mass (Lee et al., 2005).

For TEM visualization, particles were sampled directly from the laser ablation or DC arc particle generator. An electrostatic sampler was used to collect particles on 200 mesh nickel TEM grids coated with silicon monoxide. The analysis was performed with a JEOL 1210 TEM (accelerating voltage: 40–120 kV, magnification: 50× to 800,000×). Also, the differential mobility analyzer (DMA) (Knutson and Whitby, 1975) with a condensation particle counter (CPC) was used to measure particle size distribution.

Results and discussion

Particle creation, coating and characterization

Typical single particle mass spectrum for aluminum nanoparticles obtained by laser ablation or DC arc with only the argon quench is shown in Figure 3a. We observe only one peak corresponding to Al^{+1} ion, no aluminum cluster ions indicating our laser ablation is highly effective, and no oxygen indicating we are producing bare aluminum nanoparticles. In Figure 3b we show a typical mass spectrum with the argon and ethylene mixture. We observed a large aluminum peak at $m/z = 27$, and small peaks of carbon ($m/z = 12$) and hydrogen ($m/z = 1$). This suggests that the particle is composed primarily of aluminum with a small quantity of carbon and hydrogen. We found no significant difference in the mass spectrum for coated particles between the laser ablation and DC arc methods indicating that both methods have sufficient thermal energy in the gas to decompose ethylene. This simple result shows us that this approach can be used to coat aluminum nanoparticles. What remains is to determine the
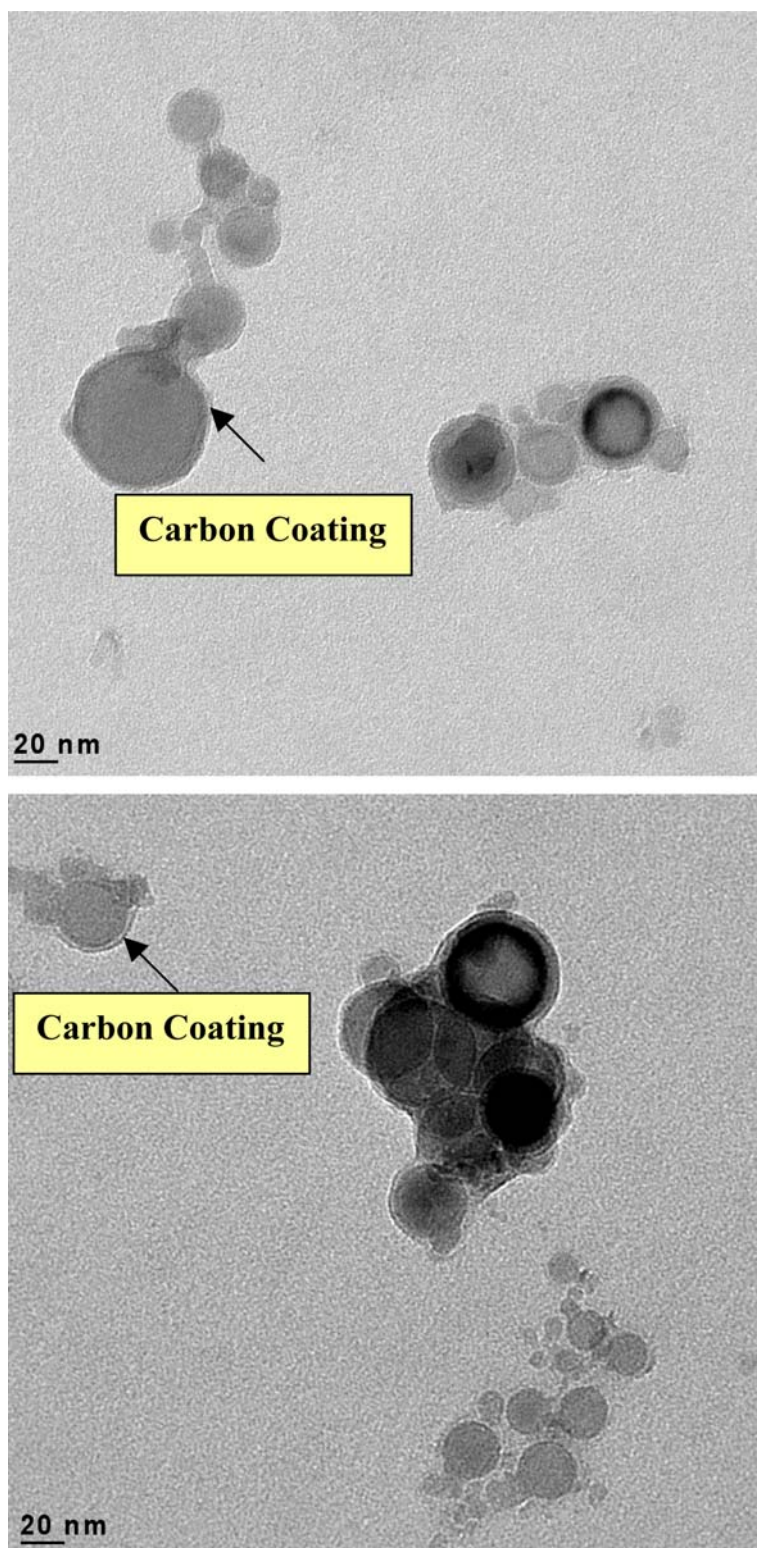
Figure 5. TEM images for coated aluminum nanoparticles obtained by DC arc method. Arrows point to carbon coating.
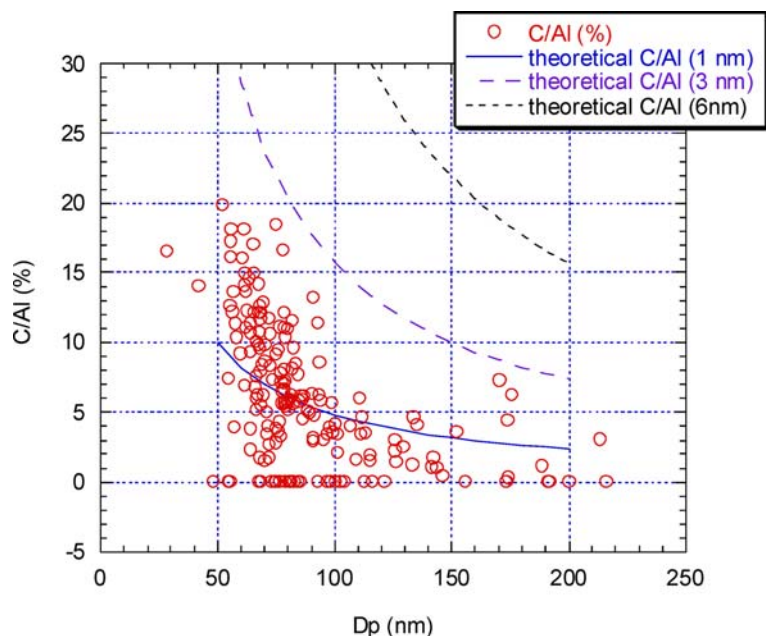
Figure 6. Measured elemental ratio (C/Al) of carbon to aluminum for coated aluminum nanoparticles as a function of particle size. Each point corresponds to a single particle. Lines are theoretically calculated values by assuming that particles are sphere and coated with a carbon film with a thickness of 1, 3, or 6 nm.

thickness of the coating achieved and how stable the coating is.

Our previous study showed that for high laser intensities we can quantitatively determine the elemental composition ratios from the mass spectra to within ∼15% (i.e., the peak area ratio in the mass spectrum linearly scales to the elemental composition ratio) (Mahadevan et al., 2002). The quantification of the elemental ratio of each element will be shown later.

A typical size distribution measured with a differential mobility analyzer (DMA) and condensation particle counter (CPC) for the coated aluminum particles is shown in Figure 4. The peak size is around 80 nm and we observed no significant difference in size distribution between the coated and uncoated particles. The corresponding TEM images of aluminum nanoparticles produced with a quench gas of argon and ethylene mixture are shown in Figure 5. As shown, these particles are slightly agglomerated, consisting of spherical primary particles, and clearly observable is a thin coating, corroborating our mass-spectrometry results. From both composition and structure information, it can be concluded that aluminum nanoparticles here are coated with a thin film of

carbon (including hydrogen), rather than integration of carbon within an aluminum matrix.

While the formation process is not the subject of this paper, and would require further investigation, our speculation and the reason for attempting the experiment in the first place is that the high temperatures in the plasma, in addition to vaporizing aluminum, would also thermally decompose the carbon source (ethylene). The reactive fragments would then heterogeneously nucleate or polymerize on any available surface (i.e. particles). This latter result implies at least qualitatively that particle nucleation is fast relative to solid carbon formation.

Since the mass-spectrometer information is quantitative in size and elemental composition, we can determine the extent of coating from the elemental ratio of carbon to aluminum and the corresponding size (Lee et al., 2005). The results are shown in Figure 6, as C/Al (mol%) as a function of particle size. Each point corresponds to a single particle measured with the SPMS. Clearly evident is the fact that as particle size decreases, the fraction of carbon increases. One can also compare the experimental results with the theoretical C/Al ratio expected for various
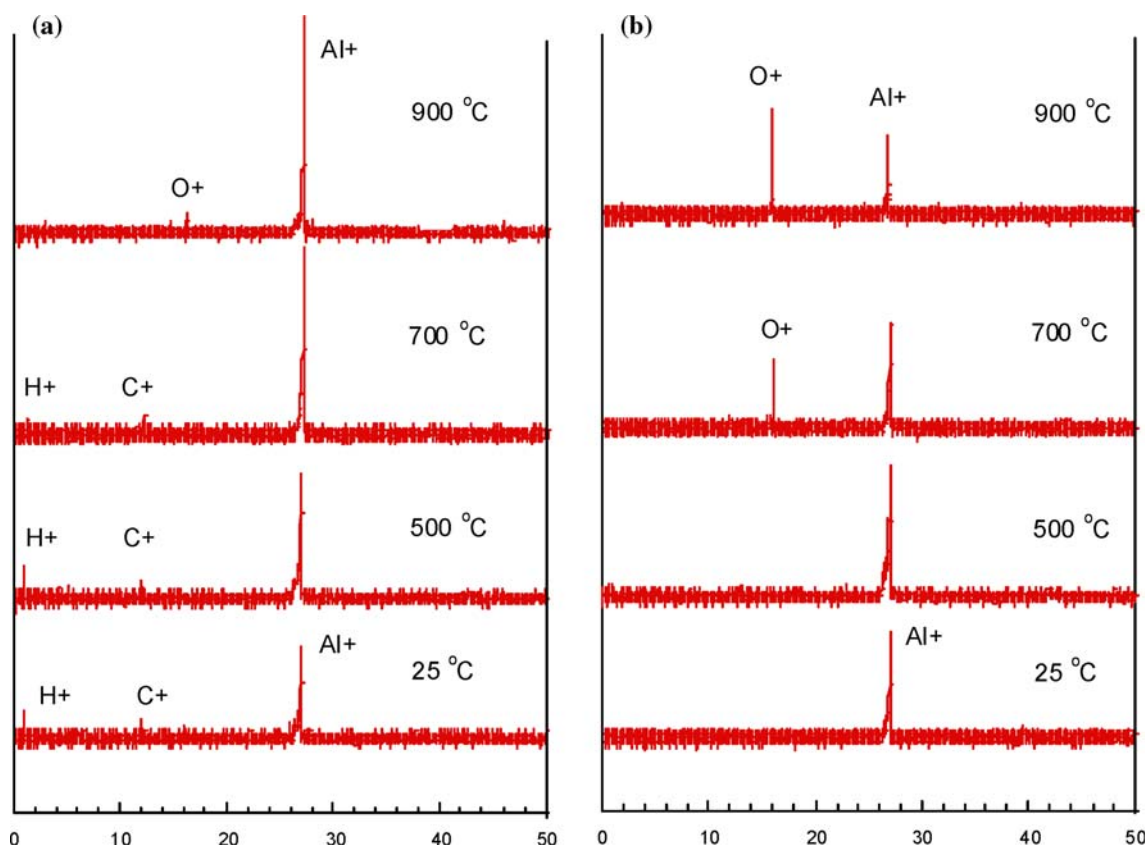
Figure 7. Single particle mass spectra as a function of temperature (25–900°C) for coated (a) and bare (b) aluminum nanoparticles heated with air in the furnace reactor.

thicknesses (e.g. 1, 3, 6 nm), presented as curves in the figure. The results suggest that the coating thickness observed experimentally falls in the 1–3 nm range, but that a few particles have no coating at all. The latter situation reflects the complex nature of the ablation process and subsequent quenching. This also indicates the value of a single particle analysis, if one were dealing with industrial scale production of such a highly reactive material.

Reactive stability

In order to examine the oxidative stability of the coated particles, we exposed the coated and bare aluminum aerosol to heated air through a tube furnace at various temperatures (residence time ~1 s). The exiting aerosol was then sampled by the SPMS. In this way we determine any change in elemental composition of coated and bare aluminum nanoparticles as a function of temperature (25–900°C). Typical mass spectrum as a function of temperature is shown in Figure 7. When the furnace temperature is increased to 700°C, no change in the elemental composition was observed for coated aluminum nanoparticles (i.e., no oxygen was detected in the particle mass spectrum) as shown in Figure 7a. This suggests that the coating successfully prevented aluminum nanoparticles from oxidizing up to at least 700°C. For comparison, we also exposed "uncoated" aluminum nanoparticles to air, and measured their elemental composition, as shown in Figure 7b. Not only is the bare particle more reactive at lower temperatures but at all higher temperatures the fraction of oxygen present was significantly higher.

In order to get the statistics of the process, we ensemble average the results for 200 particle mass spectra. We determined the relative amount of
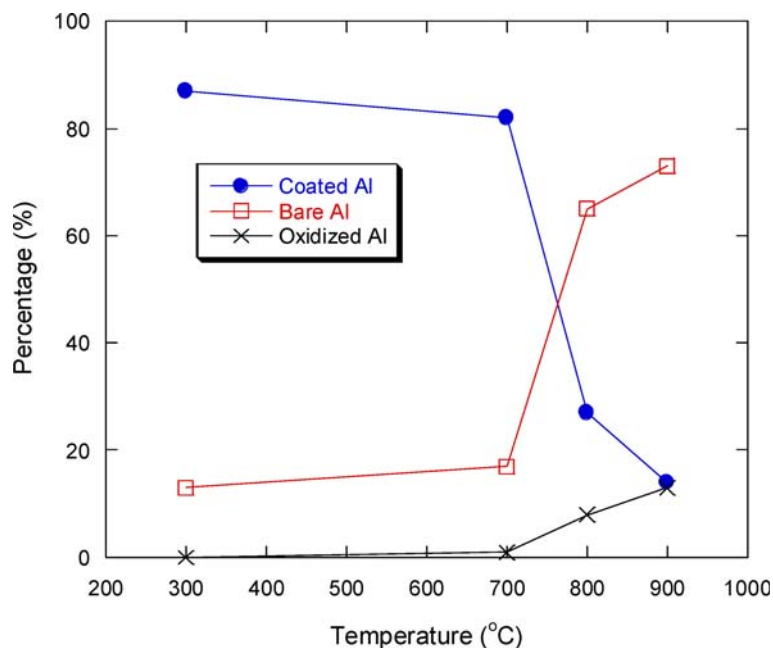
Figure 8. Relative amount of coated aluminum particles, oxidized aluminum particles, and bare aluminum particles at each temperature (average over 200 mass spectra).

coated aluminum particles, bare aluminum, and oxidized aluminum particles (i.e., oxygen containing aluminum particles without carbon) as a function of the furnace temperature. The results are presented in Figure 8, and show that as the temperature increased from 700°C to 800°C, the fraction of carbon containing particles decreased significantly, while the amount of bare aluminum particles increased. This suggests that the coating materials are stripped off the aluminum nanoparticles starting at ~800°C. This temperature is believed to be related to the oxidation temperature
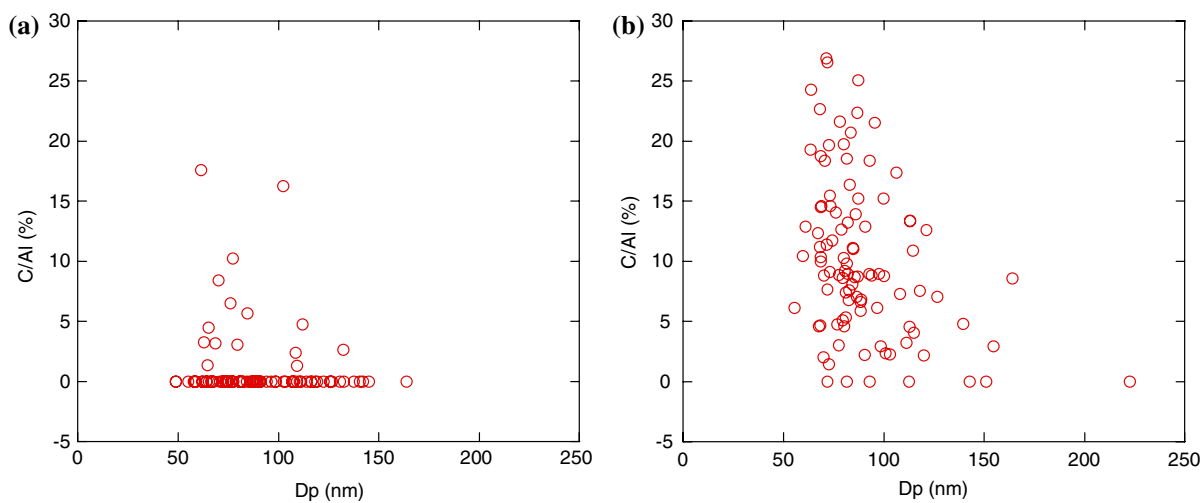

Figure 9. Elemental ratios of carbon to aluminum for the coated aluminum nanoparticles heated to 900°C after mixing with air (a) and heated in argon environment (no air) at the same condition (b).

of carbon or soot particles. Previous studies on oxidation of soot particles showed that the oxidation of soot particles started at ∼800°C (Higgins et al., 2002). Also note that the oxygen containing aluminum nanoparticles started to appear at 800°C, and their fraction increased as the temperature increased to about 900°C.

We also investigated the thermal stability of the coated particles in heated argon rather than air. Figure 9 shows a comparison of results for coated particles in air (a) and argon (b) at 900°C. The air heated samples show an almost complete loss of the carbon coating. On the other hand we found there is no detectable change in the carbon to aluminum ratio in the heated argon environment indicating that the carbon coating was thermally stable well above the melting point of the aluminum core.

Conclusions

The motivation of the work was to find an alternative surface passivating layer for nanoaluminum, which might find application in advanced propellant formulations. In this study, carbon-coated aluminum nanoparticles were produced by laser induced plasma ablation or a DC plasma arc with argon–ethylene injection downstream to create the coating. A single particle mass-spectrometer was employed to monitor the coating process, and to assess the thermal and oxidative stability of these particles.

Results showed that the aluminum nanoparticles were coated with carbon, and some hydrogen with an approximate thickness of 1–3 nm. We observed that the carbon coating was thermally stable up to at least 900°C, and that the particles were stable to oxidation below about ∼800°C. The results suggest that carbon may be a suitable candidate for surface passivation of nanoaluminum.

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