Applied Surface Science 436 (2018) 548–555

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Surface engineering of zirconium particles by molecular layer deposition: Significantly enhanced electrostatic safety at minimum loss of the energy density

Lijun Qin[a,b], Ning Yan[a,b], Haixia Hao[b], Ting An[b], Fengqi Zhao[b], Hao Feng[a,c,*]

[a] Laboratory of Material Surface Engineering and Nanofabrication, Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, People's Republic of China

[b] Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, People's Republic of China

[c] State Key Laboratory of Fluorine and Nitrogen Chemicals, Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, People's Republic of China

ARTICLE INFO

Article history:
Received 10 October 2017
Received in revised form
30 November 2017
Accepted 6 December 2017
Available online 9 December 2017

Keywords:
Molecular layer deposition (MLD)
Functional coatings
Thin films
Energetic materials

ABSTRACT

Because of its high volumetric heat of oxidation, Zr powder is a promising high energy fuel/additive for rocket propellants. However, the application of Zr powder is restricted by its ultra-high electrostatic discharge sensitivity, which poses great hazards for handling, transportation and utilization of this material. By performing molecular layer deposition of polyimide using 1,2,4,5-benzenetetracarboxylic anhydride and ethylenediamine as the precursors, Zr particles can be uniformly encapsulated by thin layers of the polymer. The thicknesses of the encapsulation layers can be precisely controlled by adjusting the number of deposition cycle. High temperature annealing converts the polymer layer into a carbon coating. Results of thermal analyses reveal that the polymer or carbon coatings have little negative effect on the energy release process of the Zr powder. By varying the thickness of the polyimide or carbon coating, electrostatic discharge sensitivity of the Zr powder can be tuned in a wide range and its uncontrolled ignition hazard can be virtually eliminated. This research demonstrates the great potential of molecular layer deposition in effectively modifying the surface properties of highly reactive metal based energetic materials with minimum sacrifices of their energy densities.

1. Introduction

High volumetric heat of oxidation makes metal fuels attractive for use in volume limited propulsion systems [1–3]. Take Zr powder as an example, Zr metal has a combustion heat of 12.0 kJ/g and a density of 6.49 g/cm^3; the volumetric energy density of Zr is 2.4 times that of gasoline (32.2 kJ/cm^3). In addition, Zr can also be used as an additive to suppress unstable combustion in double base and composite modified double base propellants and the combustion product, ZrO_2, is more transparrent to infrared detection compared to other metal oxides [4,5]. However, the application of Zr is restricted by its ultra high electrostatic discharge (ESD) ignition sensitivity, which poses great hazards for handling, transportation and utilization of this material [6,7]. Traditional methods to reduce the ESD sensitivity of an energetic material usually involve addition of conductive ingredients, such as graphite, which serve as bypasses for the dissipation of accumulated electric charges [8,9]. Besides, because the accumulation, distribution, and transportation of electric charges are closely related to the surface properties of the energetic material, surface fabrication is another effective way to mitigate the ESD ignition hazard [10–12]. The unique properties of carbon, for instance, high thermal and electrical conductivities, make it a suitable material for surface fabrication of metal fuels. The carbon layer is inert enough at room temperature and is combustible at high temperatures; and the volumetric energy density of carbon is 93.5% that of Zr. Many efforts have been made to produce carbon encapsulation layers or metal carbides on the surfaces

Abbreviations: ALD, atomiclayer deposition; MLD, molecular layer deposition; PI, polyimide; ESD, electrostatic discharge; SEM, scanning electron microscope; HRTEM, high-resolution transmission electron microscope; FTIR, fourier transform infrared; XPS, X-ray photoelectron spectroscopy; QCM, quartz crystal microbalance; TG, thermo gravimetric; DSC, differential scanning calorimetry.

* Corresponding author at: Laboratory of Material Surface Engineering and Nanofabrication, Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, People's Republic of China.

E-mail address: fenghao98@hotmail.com (H. Feng).

https://doi.org/10.1016/j.apsusc.2017.12.042
0169-4332/

of metal fuel particles for various purposes [13,14]. However, effective encapsulation of each individual metal particle with tunable, ultra thin carbon film is very difficult to achieve.

Atomic layer deposition (ALD) is an ideal thin film deposition technology capable of producing ultrathin films with high uniformity and digital thickness control [15,16]. Due to its excellent step coverage, ALD is endowed with the unique ability to fabricate substrates with irregular structures and large surface areas, such as powder systems [17,18]. Besides inorganic films, polymer films can also be synthesized through ALD approach. These processes are usually named molecular layer deposition (MLD) since in each half-reaction one monolayer of the organic molecule is deposited [19–21]. Via MLD it is possible to achieve complete encapsulation of nanoparticles by polymer layers of predetermined thicknesses, which can then be converted into carbon coatings through high temperature annealing [22–24]. The goal of this work is to establish a method to precisely fabricate polymer or carbon encapsulation layers on energetic metal particles, which will provide a pathway to effectively modify the surface properties of these materials at minimum losses of their energy densities. To the best of our knowledge, this work is the first endeavor to fabricate carbon coated energetic materials by molecular layer deposition and is the most effective method reported so far to significantly improve the electrostatic safety of Zr powder. This research demonstrates the great potential of MLD in effectively modifying the surface properties of highly reactive metal based energetic materials with minimum sacrifices of their energy densities. It can be applied to other similar materials, such as Al, B, etc., to solve their application problems associated with the surface properties.

2. Experimental

2.1. Synthesis of polyimide and carbon coatings

The commercial Zr powder was supplied by Shanghai ST-NANO Science & Technology CO., LTD, China. 1,2,4,5-benzenetetracarboxylic anhydride (PMDA, 98%, Alfa Aesar) and ethylenediamine (EDA, 99%, Alfa Aesar) were used as the precursors for polyimide (PI) MLD. Ultra pure Ar (99.999%, Xi'an Weiguang Gas Co., China) was used as the purge gas. Thin films of PI were synthesized in a homemade viscous flow hot-wall ALD reactor as described previously [25]. The deposition temperature was 160 °C. During MLD experiments the EDA container was kept at room temperature and PMDA was evaporated at 150 °C. The processing pressure was controlled at ~ 1.0 Torr. The pulse sequence used for depositing PI films on the Zr powder was 40-60-40-60 s. Following MLD, the samples were transferred into a quartz tube furnace and annealed at 600 °C for 2 h under H_2/Ar (v/v = 5/95) flow to convert the polymer coatings into the carbon coatings.

2.2. Characterization

A quartz crystal microbalance (QCM, Inficon bakeable crystal sensor) was used to monitor the film growth process during MLD experiments. The surface area of the Zr powder was determined by N_2 physisorption using a Micromeritics ASAP 2020 instrument. Thicknesses of the MLD PI and carbon films deposited on Si wafers were measured by a Horiba UVISEL spectroscopic ellipsometer. Raman spectra were collected by a Renishaw invia/reflex laser micro-Raman spectrometer with an excitation laser wavelength of 514 nm. Transmission Fourier transform infrared (FTIR) spectra were collected with a Bruker Tensor 27 FTIR spectrometer. Surface compositions of the samples were measured by a Thermo Fisher K-Alpha X-ray photoelectron spectrometer (XPS) using monochromatized Al Kα radiation (1486.6 eV). Surface morphologies and structures of the samples were characterized by an FEI Quanta 600 field emission scanning electron microscope (SEM) and an FEI Tecnai G^2 F20 high-resolution transmission electron microscope (HRTEM). Thermo gravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed using a NETZSCH STA 449C instrument. The TG-DSC measurements were conducted in the temerperature range from 50 to 1200 °C with a heating rate of 10 °C min^{-1} under air flow.

2.3. ESD sensitivity measurement

ESD ignition sensitivities of the original and the surface modified Zr samples were measured with a homemade electrostatic discharge apparatus depicted in Fig. 1. The apparatus includes a capacitor bank with capacitance varied in the range from 100 to 10000 pF. The capacitor can be charged to a voltage varied from 100 V to 26 KV. A limiting resistor (with resistance varied from 0 to 100 KΩ) is connected in series with the pin-electrode to change the range and sensitivity of the measurement. In this work the resistance was fixed at 0 KΩ to maximize the detection range. In each test, the powder sample was placed on a stainless steel cylinder affixed to a grounded base. The high voltage pin-electrode is placed 0.5 mm above the sample. Ignition was indicated by a flame or streaks of individual burning particles as the electric energy is discharged. Each sample was tested 25 times at varied capac-

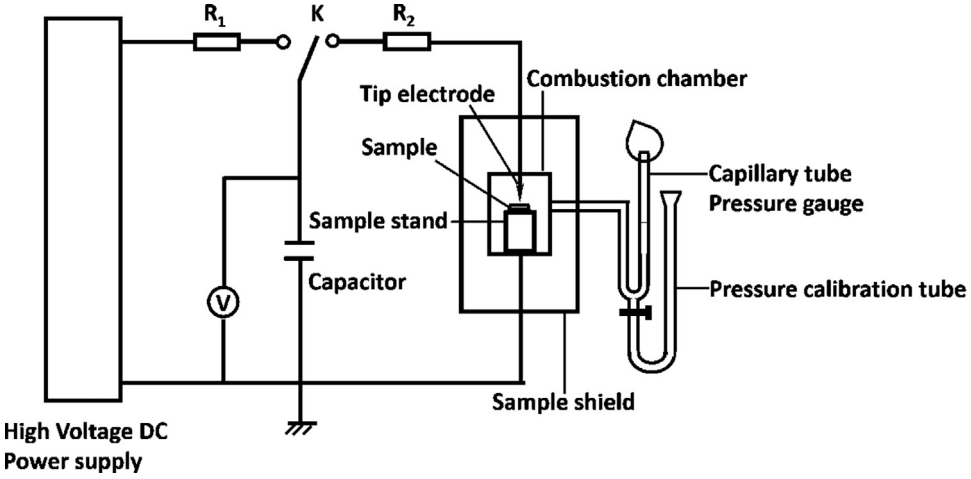

Fig. 1. Schematic diagram of the customized electrostatic discharge sensitivity measurement apparatus.