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Preparation and characterization of energetic materials coated superfine aluminum particles

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ABSTRACT

This work is devoted to protect the activity of aluminum in solid rocket propellants by means of solvent/non-solvent method in which nitrocellulose (NC) and Double-11 (shortened form of double-base gun propellant, model 11) have been used as coating materials. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to characterize the morphology of coated Al particles. Other characterization data of coated and uncoated Al particles, such as infrared absorption spectrum, laser particle size analysis and the active aluminum content were also studied. The thermal behavior of pure and coated aluminum samples have also been studied by simultaneous thermogravimetry–differential thermal analysis (TG–DTA) and differential scanning calorimetry (DSC). The results indicated that: superfine aluminum particles could be effectively coated with nitrocellulose and Double-11 through a solvent/non-solvent method. The energetic composite particles have core-shell structures and the thickness of the coating film is about 20–50 nm. The active aluminum content of different coated samples was measured by means of oxidation–reduction titration method. The results showed that after being stored in room temperature and under 50% humidity condition for about 4months the active aluminum content of coated Al particles decreased from 99.8 to 95.8% (NC coating) and 99.2% (Double-11 coating) respectively. Double-11 coating layer had a much better protective effect. The TG–DTA and DSC results showed that the energy amount and energy release rate of NC coated and Double-11 coated Al particles were larger than those of the raw Al particles. Double-11 coated Al particles have more significant catalytic effect on the thermal decomposition characters of AP than that of NC coated Al particles. These features accorded with the energy release characteristics of solid propellant.

1. Introduction

Great attentions have been focused today on ultra-fine Al particles, because of its outstanding characters and wide application in propellants, explosives and pyrotechnics. As a metal incendiary agent, it can contribute energy to the energy system [1,2]. Superfine aluminum powders (1–10 μm) which was used to replace the micronized aluminum powders (10–100 μm) in propellants, can increase the combustion efficiency of aluminum, decrease the agglomeration of combustion products, and reduce the two-phase losses [3]. However, there are significant drawbacks associated with the use of ultra-fine Al particles for energetic applications, large specific surface area and high activity of superfine aluminum, make it easy to react with steam and oxygen during storage and handing, leading to the decrease of active aluminum content [4–6].

To keep the high active aluminum content and improve the dispersibility of ultra-fine Al particles, microencapsulation technique has been used to alter the physic-chemical properties of superfine Al particles [7]. Microcapsules provide a protection shell for aluminum powders from oxygen, moisture and carbon dioxide. What is more, the microcapsule shell can be burnt quickly at high temperature and then the fresh ultra-fine Al particles were released quickly. Various materials-coated ultra-fine Al particles have been studied by many researchers, such as perfluoroalkyl ($C_{13}F_{27}COOH$) [8], polyethylene [9], transition metals [10], aluminum diboride ($Al\ B_2$) [3], Teflon [11], carbon [12], stearic acid ($C_{17}H_{35}COOH$) [13], palmitic acid [14], polymethyl methacrylate (PMMA) [15], hydroxyl-terminated polybutadiene (HTPB) [16,17], dioctyl sebacate (DOS) [6], nitrocellulose (NC) [11], etc. However, except for NC, HTPB and DOS which are components of rocket propellants, other coating materials are not energetic materials or components of rocket propellants, which may have a defect on compatibility of the different coating materials with the other compositions of propellants or decreasing of system energy. It should be pointed out that HTPB is often used as binders in rocket propellants; DOS is used as a kind of plasticizer in propellants and NC also is used as one of the compositions of modified double base propellant. Gromov [11] and Kwon [13] have used NC as coating agent to modify

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the active aluminum nanopowders by means of solvent evaporation methods. Stored the NC-coated aluminum powders in room temperature and under 70% humidity conditions for 12 months, the active aluminum content reduced to 58% from 68%, measured by gas-volumetric method. However, the solvent evaporation may leads to the agglomeration of composite particles.

In this paper, fast and controllable solvent/non-solvent method was used in the coating experiments, NC and Double-11 were used as coating materials. Nitrocellulose is a versatile polymer used as main component of propellant and high explosive formulations [18] and it has also been used as coating agent for sensitive materials and energetic materials, which has an outstanding chemical stability. Double-11 is known as one kind of double-base gun propellant, which is composed of nitrocellulose (58.5%), nitroglycerine (40.5%), centralite II (0.8%), vaseline (0.2%). The main components of Double-11 are nitrocellulose and nitroglycerine. Solvent/non-solvent method is widely used in refinement, modification of the energetic materials and preparation of composite energetic materials. The coating quality and thermal characteristics of coating Al particles have been investigated by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), grain size analysis, simultaneous thermogravimetry–differential thermal analysis (TG–DTA) and differential scanning calorimeter (DSC).

2. Experimental

2.1. Materials

Superfine aluminum powder with average particle size of 2.0 μm and the active aluminum content of 99.75%, which made by Yuan Yang Aluminum Industry Co., Ltd., China. Nitrocellulose (NC) and Double-11 used as coating materials made by lab of Nanjing University of Science and Technology, China. Amino silane coupling agents KH-550, NH_4ClO_4, NaOH, butyl phthalate (DBP) and all solvents (acetic ether, cyclohexane and ethyl alcohol absolute) were all analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Equipment and characterization

The morphology of superfine aluminum powder and coated Al particles were observed by JSM-6300 scanning electronic microscope (SEM) made by JOEL Ltd., Japan. The micrographs of coating film were characterized by Tecnai 12 transmission electron microscope (TEM) made by Philips, the Netherlands. The Fourier transform infrared (FTIR) absorption spectrums of coated aluminum particles and pure NC and Double-11 were measured by Nicolet IS-10 instrument and the IR data were collected in the range of 500–4000 cm^{-1}. Particle size and size distribution of coated and uncoated samples were measured by Mastersizer Microplus Instrument, by Malvern Ltd., England. The thermochemical behavior of raw Al particles and coated samples was characterized by TG–DTA and DSC methods. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out by HCT-2 Instrument, by Beijing Henven Scientific Ltd., China. The conditions of TG–DTA are as follows: with an Al_2O_3 crucible, from 30 °C to1000 °C with a heating rate of 20 °C/min, under air atmosphere. The TG–DSC curves were obtained by Netzsch differential scanning calorimeter model STA 449C, in the temperature range of 30–1000 °C, at a heating rate of 20 °C/min, under air atmosphere with the flow rate of 20 ml/min. The DSC curves of pure AP and mixture of coated Al particles and AP were obtained by Mettler Toledo differential scanning calorimeter model 823e, in the temperature range of 40–500 °C using an aluminum crucible, at a heating rate of 20 °C/min, under nitrogen atmosphere with the flow rate of 20 ml/min. The average sample weight was about 5.0 mg.

2.3. Coating procedures

2.3.1. Pretreatment of raw aluminum powders

A proper amount of superfine aluminum powder was added to 0.01 mol/l NaOH solution to remove the oxide layer. The consumption amount of NaOH solution is decided by the content of active Al of raw material, which was determined by means of oxidation–reduction titration according to the national military standard GJB 1738–1993 of China. The reaction equation as follow: $Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$. The treated ultra-fine Al particles with high activity were stored in ethyl alcohol absolutely. The ethanol solution of amino silane KH-550 (KH-550 weight based on aluminum powder weight is 5%) was added to the pretreated fresh Al powder immediately, the powder suspension was mechanically stirred at 60 °C for 2 h under nitrogen atmosphere, in order to avoid oxidation of the Al powder. Finally, the modified aluminum powders were filtered and vacuum dried at 45 °C for 12 h.

2.3.2. Solvent/non-solvent method

Solvent/non-solvent was one alternative microencapsulation procedure which works based on the coacervation principle [19]. In representative experiments, 0.15 g NC and DBP (10% weight of NC) dissolved in 50 ml acetic ether with the help of ultrasonic dispersion. The concentration of NC in acetic ether solution is 4 g/l. Then, the solution was added to the container involving 2 g of the aluminum powder modified by KH-550, the solution was heated in water bath to 40 °C under nitrogen atmosphere. After 30 min of mixing under 200 rpm stirring with a magnetic stirrer, the mixture was added to 250 ml cyclohexane slowly with vigorous stirring and ultrasonic dispersion. In which cyclohexane acted as non-solvent for NC. The temperature of cyclohexane was room temperature (20 °C) and the addition speed of the mixture was 2 ml/min. The addition of mixture results in the precipitation of NC out of ethyl acetate solution. The precipitated NC stuck to the surface of aluminum powder and formed the desired coating layer. Reaction time was 50 min at room temperature under nitrogen atmosphere after the addition of mixture was over. Then, the coated aluminum particles were filtered and washed with cyclohexane two times and dried at 50 °C under vacuum conditions.

The coating technology of Double-11 is similar to that of NC, except that the acetic ether solution of Double-11 was prepared without adding DBP.

2.3.3. The composition of AP and the coated samples

In solid rocket propellants, ultra-fine Al particles were often used as metal incendiary agent and AP used as oxidant. The mixing of Al and AP can simulate the combustion performance of rocket propellants. In a representative experiment, 1 g of AP was slurred in 50 ml alcohol–water solution (volume ratio is 1:2), 0.2632 g of 5% NC-coated (NC by weight with respect to Al powder) Al powder or Double-11-coated Al powder was added to the alcohol–water solution. The mixture was turbulently mixed at a stirring rate of 120 rpm with a magnetic stirrer. The solvent phase was removed by distillation under reduced pressure, the mixed solid phase was vacuum dried at ambient temperature and the mixture of AP and coated Al particles was achieved.

3. Results and discussion

3.1. Results of SEM and TEM analysis

Morphological investigation of microencapsulated particles, through SEM and TEM analysis, proper information about coating