

COMBUSTION PERFORMANCE OF Ni-COATED AND UNCOATED HIGH ENERGETIC ALUMINUM NANOPARTICLES

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Abstract: High energetic aluminum nanoparticles are mainly used as additive in solid rocket propellants. However, fabrication of these aluminized energetic materials is associated with decreasing the burning rate of propellants due to problems such as oxidation and agglomeration of nanoparticles. In this study, to improve combustion performance of aluminum nanoparticles, coating by metallic Ni shell was studied. Nickel coating of aluminum nanoparticles was performed through electroless deposition (ED); subsequently, morphology and chemical composition of Ni-coated nanoparticles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). These studies show that a uniform Ni layer with a thickness of 10nm is coated on the surface of Al nanoparticles. Thermal analysis of uncoated and Ni-coated aluminum nanoparticles was done using differential thermal analysis (DTA) and thermo gravimetric analysis (TGA). The results of thermal analysis indicate that, coating the aluminum particles by Ni, leads to improvement in combustion performance of aluminum nanoparticles through decreasing critical ignition temperature, ignition delay time of the nanoparticles and promoting the ignition by exothermic chemical reactions between Al and Ni.

Keyword: Combustion mechanism, Aluminum nanoparticle, Electroless deposition, Electron microscopy.

1. INTRODUCTION

Aluminum powders are usually added to solid rocket propellants; due to their tendency to increasing specific impulse and energetic characteristics of rocket propellants[1, 2]. However, the applications of such additives in energetic materials are accompanied with some limitations. Aluminum oxide layer, which is formed due to oxidation of particles surfaces at lower temperatures, leads to increasing the ignition temperature of the particles. On the other hand, aluminum particles in an oxidizing atmosphere, typically ignites only after heating at temperatures close to the melting point of alumina at 2300 °K[1, 3]. In addition, agglomeration of Al particles in the propellant surface layer leads to incomplete combustion of Al and slag formation inside the solid rocket motor. As a result of mentioned limitations, due to increase in burning time or decrease in burning rate of aluminized energetic materials, combustion efficiency of these materials are reduced [1].

In recent years, different methods for improving combustion behavior of aluminized energetic materials are introduced; application of aluminum nanoparticles with more specific area and reactivity, addition of activated metals such as magnesium, addition of modifying agents to the propellants and coating the surface of Al particles with various organic or inorganic materials are some suitable methods for improving combustion behavior of aluminized energetic materials[2]. Among these methods, coating the aluminum nanoparticles has been reported as a more effective method. It is also demonstrated that the thermal characteristics of inorganic coatings for aluminum nanoparticles was more appropriate compared to organic coatings[4, 5]. Coating the aluminum particles with an inorganic thin film was recognized as a useful method for improving combustion performance of aluminized energetic materials through preventing particles agglomeration and increasing the oxidation stability in air during storage period [1, 3, 4, 6].

In this study, coating the aluminum

nanoparticles with nickel thin films is investigated. Nickel coating on particles can be achieved through different methods of electro deposition and electroless deposition (ED). However, electroless deposition is recognized a more effective technique due to its advantages such as lower costs with simple processing, easy control of coating thickness, uniformity of deposits on complex shapes and independency from substrate's electrical properties [7-15]. So far, no article about coating the Al nanoparticles by ED has been reported. Morphology and phase evaluation of Ni-coated aluminum nanoparticles investigated in the current research and subsequently, thermal behavior of Ni-coated and uncoated aluminum nanoparticles were studied using differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) techniques.

2. EXPERIMENTAL PROCEDURES

Table 1 shows the main chemicals and their concentration in the electroless nickel bath. In this research, nickel sulfate ($\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$) was used as the main salt. In addition, sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) as the reducing agent and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$) as the complexing agent are other components.

Initially, 10g of aluminum powders was fed into a solution of sodium hypophosphite in distilled water (80 °C), while the magnetic stirrer was used for stirring the bath avoid particle agglomeration. After that, nickel-complex solution was fed into the suspension. Subsequently, different buffering agents of ammonium chloride (NH_4Cl), sodium hydroxide (NaOH) and ammonia (NH_3) was added to the bath, to control the pH at 9.5.

Table 1. Main chemicals and their concentration in electroless nickel bath

Chemical	Concentration
Nickel sulfate ($\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$)	0.07 mol/l
sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	0.245 mol/l
sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$)	0.098 mol/l
ammonium chloride (NH_4Cl)	2ml/l
sodium hydroxide (NaOH)	2.5g/l
ammonia (NH_3)	5ml/l

At this situation, nickel starts deposition in the bath by changing the bath color to dark and releases the hydrogen gas (H_2). Nickel deposition is rapid at the initial stages of process and then gradually decreases. However, it seems that, after 30 minutes of deposition, the deposition process has finished.

The coated particles are separated by centrifugation from the bath; washed in distilled water for several times and finally dried in a vacuum oven at 80 °C for 3 h.

The morphology, thickness, uniformity, and chemical composition of the fabricated Ni-coated aluminum nanoparticles are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) were done by Unisantis XMD300 instrument with Cu-K α radiation ($\lambda = 1.5402 \text{ \AA}$). Also, in order to investigate thermal behavior of uncoated and Ni-coated aluminum nanoparticles, differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were performed using the BAHR STA 503 Instruments. The experiment conditions were: starting at room temperature to final temperature of 1000 °C; heating rate: 10 °C/min, air atmosphere, reference material: Al_2O_3 (35.5mg) and sample weight: $35.5 \pm 1 \text{ mg}$.

3. RESULTS AND DISCUSSIONS

Fig. 1a shows the SEM images of aluminum particles before electroless plating. As received Al particles were spherical with mean particle size of about 90nm. On the other hand, as indicated in Fig. 1b, Ni-coated aluminum particles are uniform in shape and size and no agglomeration of aluminum particles are observed in the micrograph. Preventing the particles agglomeration through electroless nickel deposition, can lead to improving materials burning process. It can be explained by the fact that the melting point of Ni (1728 °K) is much higher than that of Al (933 °K). The solid Ni layer on the surface of Al droplets prevent the coalescence and agglomeration of the burning propellants[6].

Also, the uniformity and thickness of the Ni-

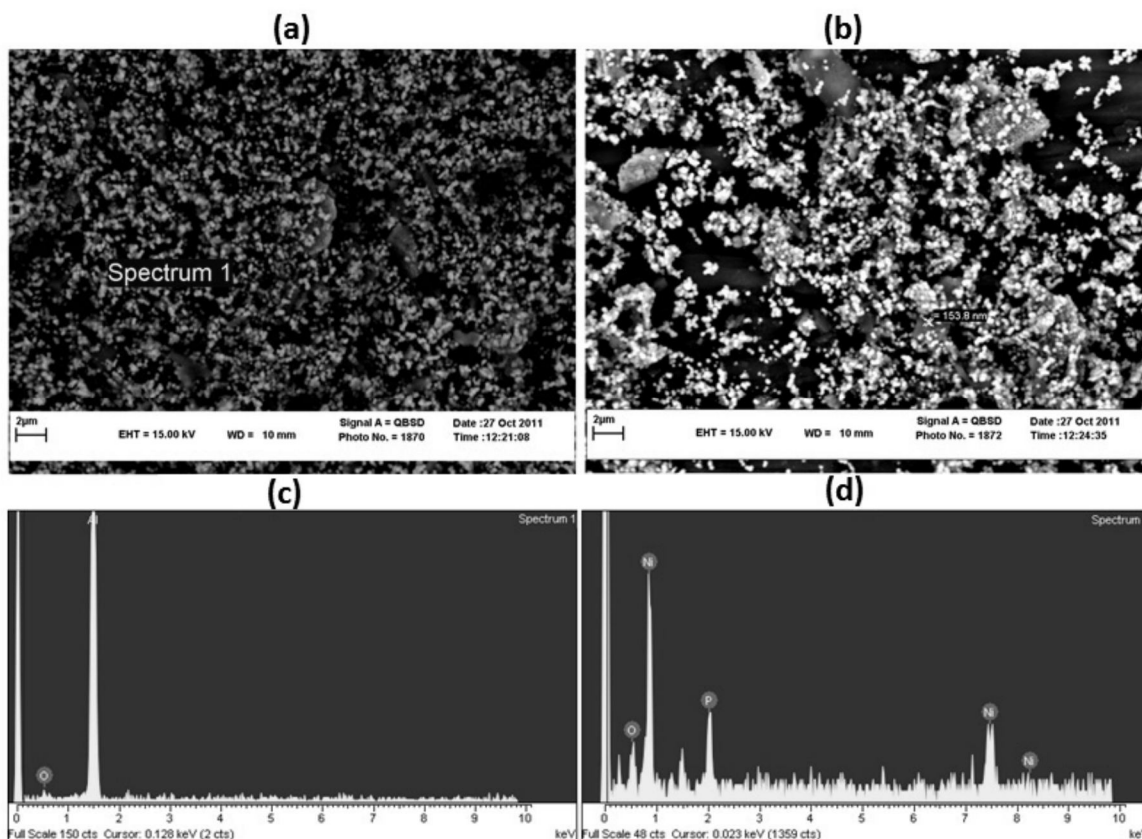


Fig. 1. (a) SEM micrograph of Al particles, (b) SEM micrograph of Ni-coated Al particles (c) EDS pattern of Al particles, and (d) EDS pattern of Ni-coated Al particles

coated aluminum nanoparticles has been studied by TEM micrograph. As shown in Fig. 2; a thin, uniform and continuous nickel shell with a thickness about 10nm was coated on the surface of aluminum nanoparticles.

The EDS profile of uncoated aluminum particles in Fig. 1c shows that the composition of initial particles is aluminum element, with small amount of oxygen related to surface oxidation of fine aluminum particles. However, according to Fig. 1d, the coated particles composition is mainly nickel, while small amount of phosphor and oxygen is present in the shell composition.

Figure 3 shows the XRD patterns of Ni-coated aluminum particles. Both Al and Ni peaks are appeared in the pattern, which confirms deposition of Ni on the aluminum particles. It should be noted that, because of the use of alkaline bath for experiments, low amounts of phosphorus and crystalline deposits can be obtained. In this pattern, no peaks of aluminum

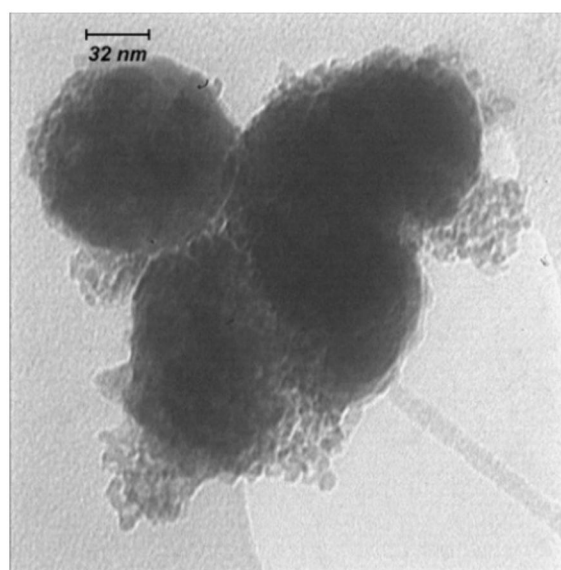


Fig. 2. TEM micrograph of Ni-coated aluminum nanoparticles

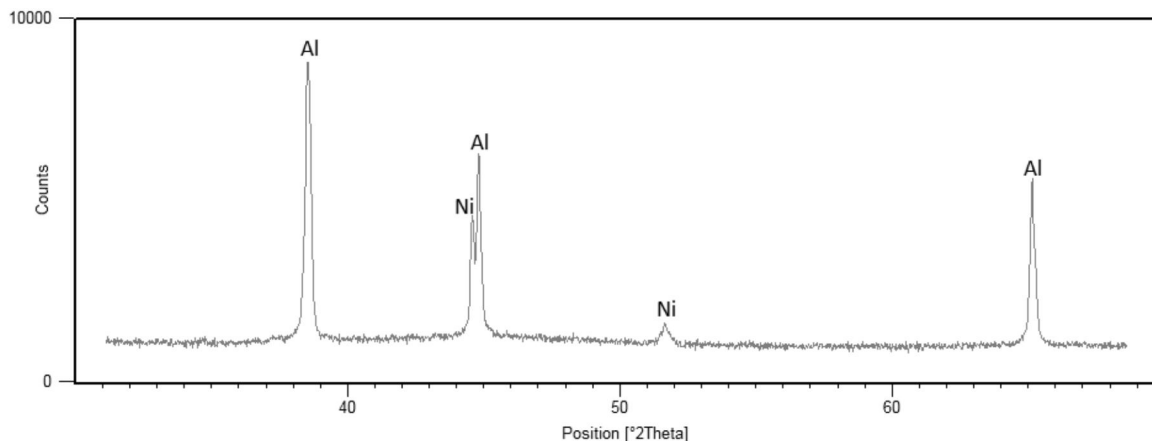


Fig. 3. XRD pattern of Ni-coated Aluminum particles

oxides or nickel oxides are detected; which indicates that surface oxidation has not occurred during the particles agitation in the hot and aqueous electroless bath; and also during the drying step in furnace.

TGA curve of Al nanoparticles is illustrated in Fig. 4a. As shown, the sample's weight is increased with increasing the temperature. The sample's Weight increasing can be explained by the absorption of atmospheric oxygen and the oxidation of Al nanoparticles. Therefore, the curve shows the oxidation mechanism of the Al nanoparticles[3]. According to the changes in the slope of diagram, oxidation mechanism of Al

nanoparticles can be explained using the following stages:

Stage 1 (up to 500-600 °C): low rate oxidation of the particles surfaces at the atmospheric air.

Stage 2 (from 600 to 650 °C): Increasing in the oxidation rate of Al particles is due to increasing the temperature. At these temperatures, the amorphous aluminum oxide layer with thickness up to 4nm as a continuous shell around the Al nanoparticles is formed.

Stage 3 (from 650 to 800 °C): Aluminum oxide layer around the Al particles acts as a barrier against diffusion of oxygen to the surface of Al nanoparticles and decrease the oxidation rate. At

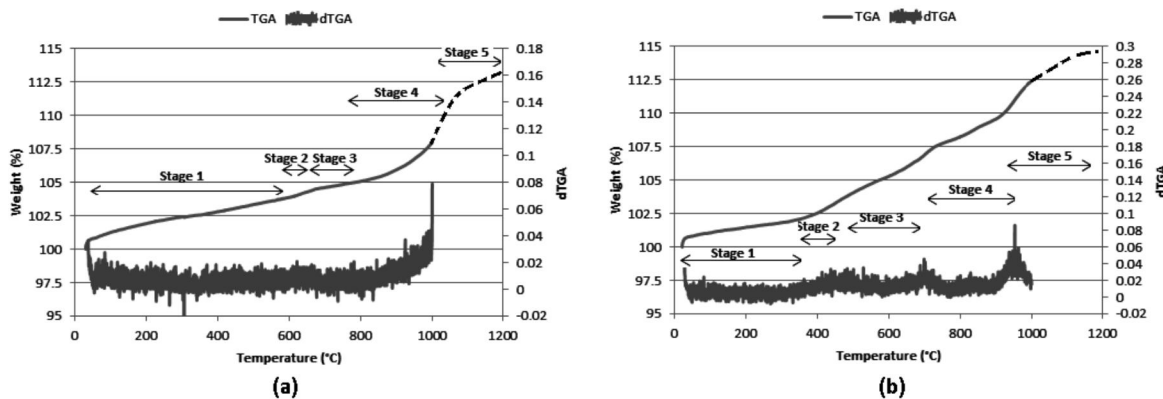


Fig. 4. TGA curve of a) uncoated Al nanoparticles, b) Ni-coated nanoparticles

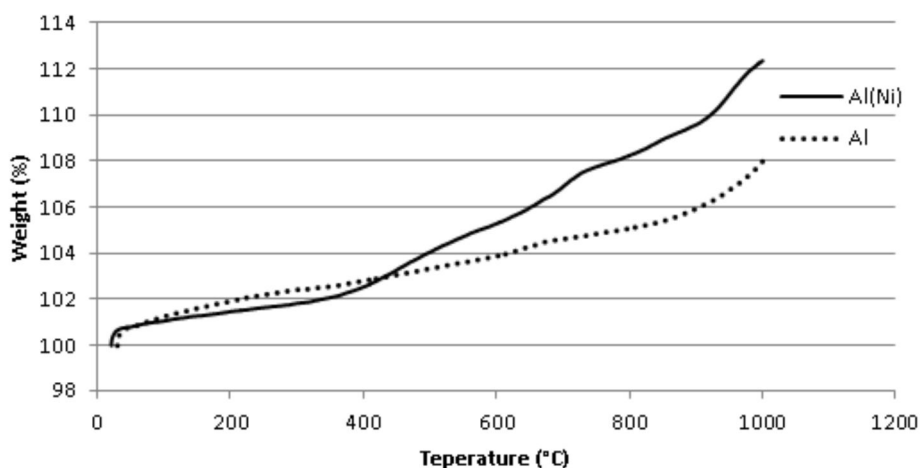


Fig. 5. Comparative TGA curves of uncoated and Ni-coated Al nanoparticles

this step, by increasing the thickness of aluminum oxide layer, amorphous aluminum oxide converts to δ - aluminum oxide.

Stage 4 (from 800 to 1100 °C): increase in oxidation rate of the Al particles due to eventual cracking of the δ - aluminum oxide layer and therefore more oxidation of Al nanoparticles because of more diffusion of oxygen through the cracks. At this step, δ - aluminum oxide converts to θ - aluminum oxide layer.

Stage 5 (From 1100 °C): Conversions of θ - aluminum oxide layer to the more stable α - aluminum oxide layer. In this step, due to the formation of more stable and denser aluminum oxide layer, oxygen diffusion to the surface of Al nanoparticles reduced; therefore the oxidation rate decreased.

Stage 6 (about 2000 °C): ignition of aluminum particles, after melting of stable α - aluminum oxide layer at temperatures close to 2000 °C.

According to these results, critical ignition temperature and ignition delay time of Al nanoparticles have been increased due to the formation of aluminum oxide layers on the surface of particles. In addition, combustion rate of particles has been decreased leading to the increase of total time of particles combustion.

TGA curve of Ni-coated aluminum nanoparticles is shown in Fig. 4b. Similar to combustion of Al nanoparticles, combustion mechanism of Ni-coated Al nanoparticles

consists of different stages[3]:

Stage 1 (up to 350 °C): Low rate oxidation of nickel on the surface of particles.

Stage 2 (from 350 to 420 °C): Increasing oxidation rate of nickel is due to increasing temperature. Comparing with TGA curve of Al nanoparticles, the onset temperature of the first oxidation process occurs at much lower temperatures for Ni-coated particles.

Stage 3 (from 420 to about 660 °C): Oxidation of Ni occurs at a faster rate due to larger effective surface area of Ni layer and porous nature of oxide layer.

Stage 4 (from 660 to about 1000 °C): In this stage, the nickel oxide layer on the surface of Al nanoparticles cracks due to thermal expansion of the liquid Al core. At such temperatures, easy ignition of Al nanoparticles starts. Besides, due to high exothermic reaction between Al and Ni at this temperature period, ignition property of particles significantly improves.

Effects of Ni coating on the combustion behavior of energetic Al nanoparticles can be realized according to discussed combustion mechanisms and comparing TGA curves of uncoated and Ni-coated Al nanoparticles (Fig. 5).

The results indicated that the Ni coating significantly decreases both critical ignition temperature and ignition delay time of the Al nanoparticles.

Burning rate of Ni-coated Al nanoparticles is

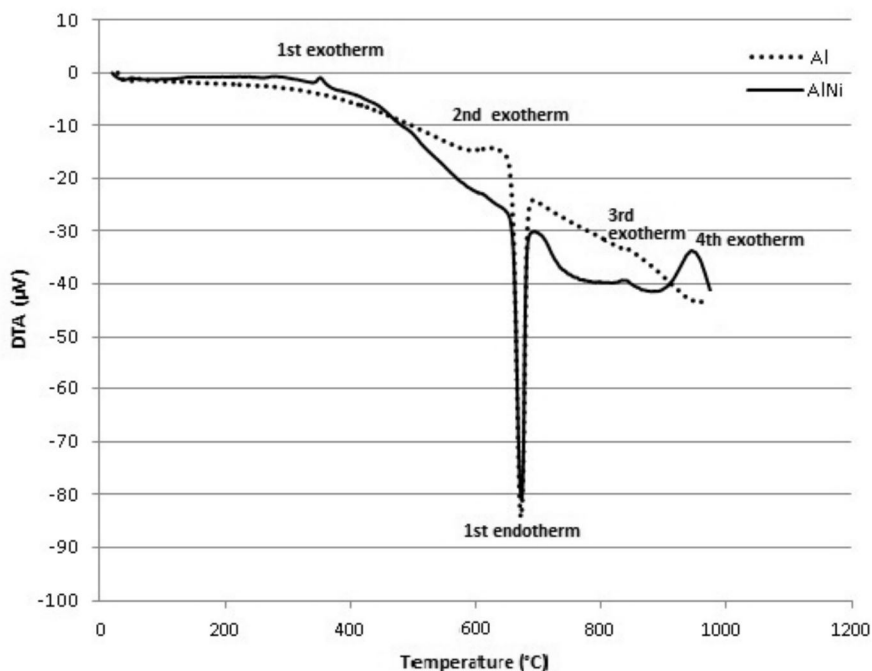


Fig. 6. DTA curves of uncoated and Ni-coated Al nanoparticles

increased leading to easier ignition and decreasing of total combustion time. In addition, exothermic reactions for formation of intermetallic Ni_3Al play a major role in increasing combustion energy and flame temperature.

Figure 6 shows the DTA graphs of uncoated and Ni-coated Al nanoparticles. At temperature about 370 °C first exothermal reaction is identified in the DTA graph of Ni-coated particles. The larger enthalpy produced in this temperature is mainly due to the oxidation of Ni to NiO. Otherwise, oxidation of Al particles was performed at temperature about 600 °C in the DTA graph of uncoated particles. At temperature about 660 °C large endothermal peak related to Al particles melting was observed. On the DTA graph of Ni-coated particles another exothermal peak was detected at temperature about 840 °C. It is reported that exothermic reaction for formation of intermetallic Ni_3Al is done at such temperatures[3]. As discussed before, due to the breakage of the protective aluminum oxide layer at temperatures about 850 °C rapid oxidation of the Al nanoparticles was performed. For Ni-coated

particles, ignition of particles started at temperature of about 1000 °C. The high exothermal peak on the DTA graph of Ni-coated particles indicates the starting point of particles ignition.

4. CONCLUSIONS

1. In order to improve Combustion performance of Al nanoparticles, uniform and continuous Ni layer with 10nm thickness coated on the surface of Al nanoparticles through electroless deposition.
2. Ni coating significantly decreases both critical ignition temperature and ignition delay time of the Al nanoparticles.
3. Before temperature of about 400 °C oxidation rate of Ni-coated particles is much lower than uncoated particles, causing increase stability to oxidation in air during the storage period.
4. Burning rate of Ni-coated Al nanoparticles is higher compared to uncoated particles, which leads to easier ignition and decreasing in total combustion time of Al particles.

5. Exothermic reactions for formation of intermetallic Ni₃Al play a major role in increasing combustion energy and flame temperature of Al particles ignition.

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