

Ti-alloys: Potential nano-modifier for Rocket Propellants

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ABSTRACT: Composite solid propellants were prepared with and without nano-alloys (Ti-Co, Ti-Ni, Ti-Zn), where nano-alloys used as catalyst. These Nano-alloys are prepared by Hydrazine reduction method. Catalytic properties of these nanomaterials were measured on Ammonium perchlorate / Hydroxyterminatedpolybutadiene propellant by Thermogravimetry analysis and Differential thermal analysis. Both experimental results show enhance in the thermal decomposition of propellants in presence of nano-alloys. In this Differential thermal analysis method experiments had done in 3 heating rate $\beta_1=5$, $\beta_2=10$, $\beta_3=15$ degree on minute. Independent to model free; calculation of activation energy of high temperature decomposition step was done by using following Kissinger equation. Burning rate of propellants is also calculated.

Keywords: Activation energy; Ammonium perchlorate; Burning rate; Propellants; Thermal decomposition

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INTRODUCTION

Composite solid propellants (CSPs) are a self sustaining combustible material containing both fuel and oxidizer in a solid state. They are widely used in several applications such as gas generators for airbags, propulsion for large space vehicles and tactical missiles, attitude control systems and as pressure generators in deep sea oil operations. The most common oxidizer used in CSPs is ammonium perchlorate (AP) [1-4]. Thermal decomposition characteristics of AP influence the combustion behavior of the propellant. Burning rate of the solid propellants is an important parameter because it is directly related to the performance of the propellant. In CSPs, the burning rates of AP are routinely adjusted by the addition of small amounts of burning rate catalysts to the propellant formulation. Burning rate catalysts are not only a ballistic nature regulator in the solid propellant, but also an absolutely necessary ingredient because of their ability to enhance the

burning character and to eliminate the primary smoke of the propellant. So, burning rate catalysts have attracted considerable attention. A comprehensive survey of the literature on burning rate catalysts suggests that the burn rate depends on catalyst concentration, surface area, particle size and state of aggregation [5, 6]. Hence, for achieving a large surface area, a new class of catalysts based on ultrafine particles i.e., nanoparticles (NPs) were developed. The burn rate modifier catalyzes the decomposition of oxidizer and its smaller particle size enhances the catalysis in the gaseous phase of the combustion. The optimum concentration of these catalysts produces effective results. High burning rate CSPs are needed for future programmes: particularly in surface to air mission to reduce the operational time of the missiles.

Nowadays, the main burning rate catalysts for CSPs are nanosized like nano-alloys. NPs without any agglomeration can increase the burning rate of propellants [7, 8]. The efficiency of catalytic action increases sharply in nano particles than micro scale

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particles [1-4 and 7, 8]. Pure metal and alloy NPs are much sensitive to oxygen and may be effective to improve the decomposition efficiency of AP [1-4]. Owing to their small particle size, large specific surface area, electronic effect and lattice defects, nano metals endow burning rate catalysts with good chemical reactive properties.

In this article we prepare composite solid propellants (CSPs). Bimetallic nano-alloys (Ti-Co; Ti-Zn; Ti-Cu) are used as additive. Thermal decomposition of propellants was studied using TGA/DTA analysis. Activation energy was calculated by Kissinger equation and Burning rate was also calculated.

EXPERIMENTAL

Preparation of BMNs

All BMNs were prepared as reported earlier [9]. An appropriate amount of metal chloride (2.5-45 mM) was dissolved directly in ethylene glycol followed by addition of an appropriate amount of hydrazine (0.05-0.9 M) and of 1.0 M NaOH solution (10- 72 μ L). At 60 °C, metal NPs were formed after about 1 hr in a capped bottle with stirring. The reaction was performed in an organic solvent instead of aqueous solution, so it was relatively easy to form pure metals. Nitrogen gas was produced and bubbled up continuously during reaction which created an inert atmosphere and hence the passing extra N₂ gas was not necessary for the synthesis of pure BMNs.

Characterization

Characterizations of BMNs were carried out using powder XRD and SEM techniques (Fig. 1, 2). X-ray diffraction (XRD) measurement were performed on the BMNs by an X-ray diffractometer using CuK α radiation ($\lambda = 1.5418$). The diffraction pattern is shown in Fig. 1. Particle size was calculated by applying Scherrer's equation [10]. SEM (JEOL-JSM6510LV) images are shown in Fig. 2.

Preparation of CSPs

CSP samples were prepared by dry mixing [11] of AP [100-200 and 200-400 mesh (3:1)] with BMNs (1% by wt.). The solid materials were mixed with HTPB in the ratio of 3:1. The binder part includes the curing agent (IPDI) in equivalent ratio to HTPB and plasticizer (DOA, 30% to HTPB). During mixing of the solid components with HTPB, temperature was maintained

at 60 °C for 1 hr. The propellants were prepared with and without BMNs, casted into aluminium plates having dimensions 1x 3x 10 cm³. The samples were cured in an incubator at 70 °C for 10-15 days [12]. An average of 3 measurements was taken which are within experimental error and results are reported in Table 1.

Measurement of Burning Rate

The cured propellant samples were cut into smaller pieces having dimensions 0.8cm \times 0.8cm \times 9.0cm and burning rate was measured at ambient pressure by fuse wire [12] technique. An average of 3 measurements was taken (See Table 1).

TGA/DTA Analysis of Propellants

The non-isothermal decomposition of propellants with and without BMNs were carried out in static air using indigenously fabricated TG apparatus at a heating rate of 10 °C/min in N₂ atmosphere taking 20mg of samples. The plots of TGA and DTA analysis are shown in Fig. 3 respectively.

In this, experiments were carried out in 3 heating rate $\beta_1=5$, $\beta_2=10$, $\beta_3=15$ degree on minute. Independent to model free; calculation of activation energy of HTD step was done by using following Kissinger equation [13].

On differentiation

$$\frac{d \ln [\beta/T^2 \max]}{d[1/T \max]} = \frac{(-E)}{R} \quad (1)$$

Table 1: Burning rate of CSPs with and without BMNs (1% by wt.)

Sample	Burning Rate (mm/sec)	r*/r
CSP	4.90	1.00
CSP+Ti-Co	3.47	1.41
CSP+Ti-Ni	2.90	1.69
CSP+Ti-Zn	4.05	1.21

r* and r is burning rate of CSP with and without BMNs respectively.

Table: 2 Activation energy of HTD step.

Sample	Activation energy (E) (kJ/mol)
CSP	116.172
CSP+Ti-Co	92.630
CSP+Ti-Ni	99.160
CSP+Ti-Zn	97.370

$$\ln [\beta/T_{\max}^2] = (-E)/RT + \text{Constant} \quad (2)$$

Where B , E , R and T are the heating rate, activation energy, gas constant and a specific temperature, respectively. A plot of $\ln(B/T^2)$ versus $1/T$ yields an approximate straight line with a slope of $-E/R$ (Fig. 4 and Table 2).

RESULTS AND DISCUSSION

XRD results are displayed in Fig. 1 for 2θ angle values of 10–100. An XRD result shows amorphous nature of Ti-Co particles while Ti-Zn and Ti-Ni particles are sharp crystalline in nature. SEM image of Ti-Ni shows cluster of spikes while Ti-Zn has needled shaped. Particle size was calculated via

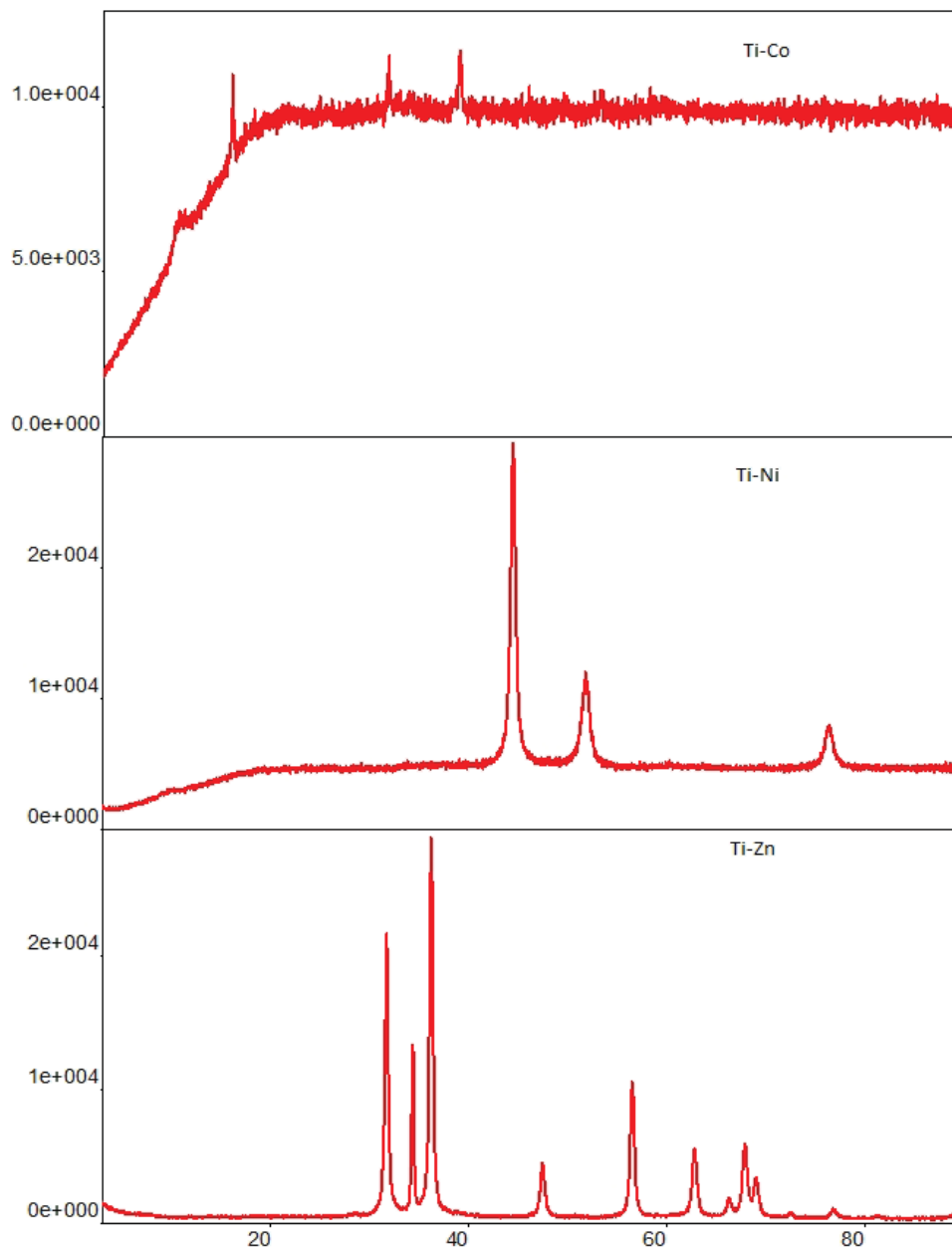


Fig. 1: XRD of Alloys a) Ti-Co b) Ti-Ni c) Ti-Zn

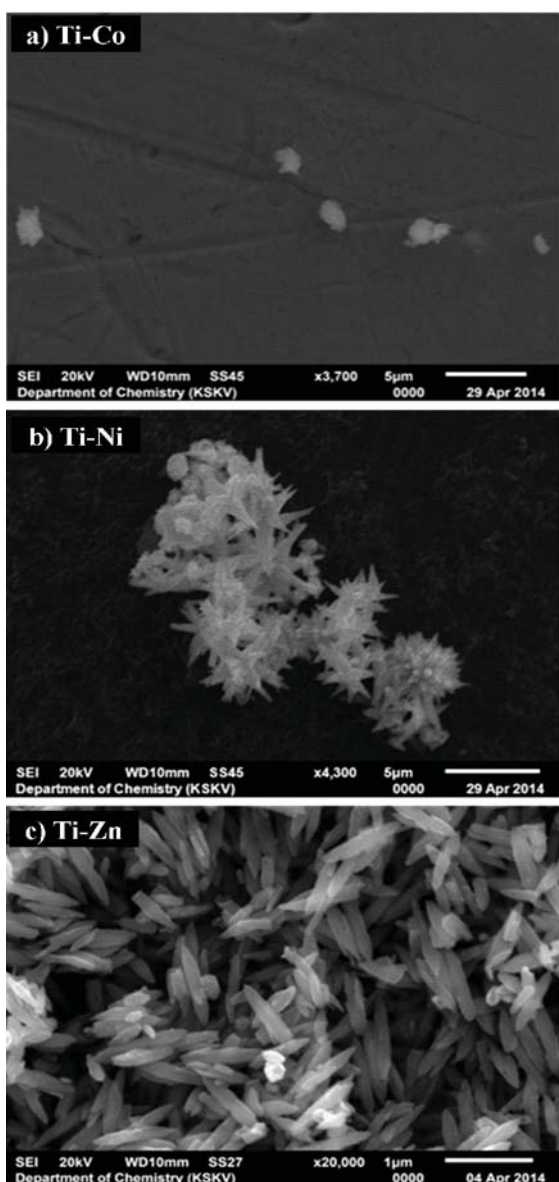


Fig. 2: SEM of Alloys; a) Ti-Co, b) Ti-Ni; c) Ti-Zn

Scherrer's equation [14]. Particle size 28.2, 16.1 and 24.6 nm for Ti-Co, Ti-Ni and Ti-Zn respectively.

Most of the studies suggested that ballistic modifiers are active mainly in the condense phase at AP-binder interface [15]. TG and DTA shown in Fig. 3 indicates that the condensed phase reactions are occurring in CSPs. CSPs has two step decomposition namely LTD and HTD whereas in case of propellants with BMNs, LTD almost disappear while HTD occurs

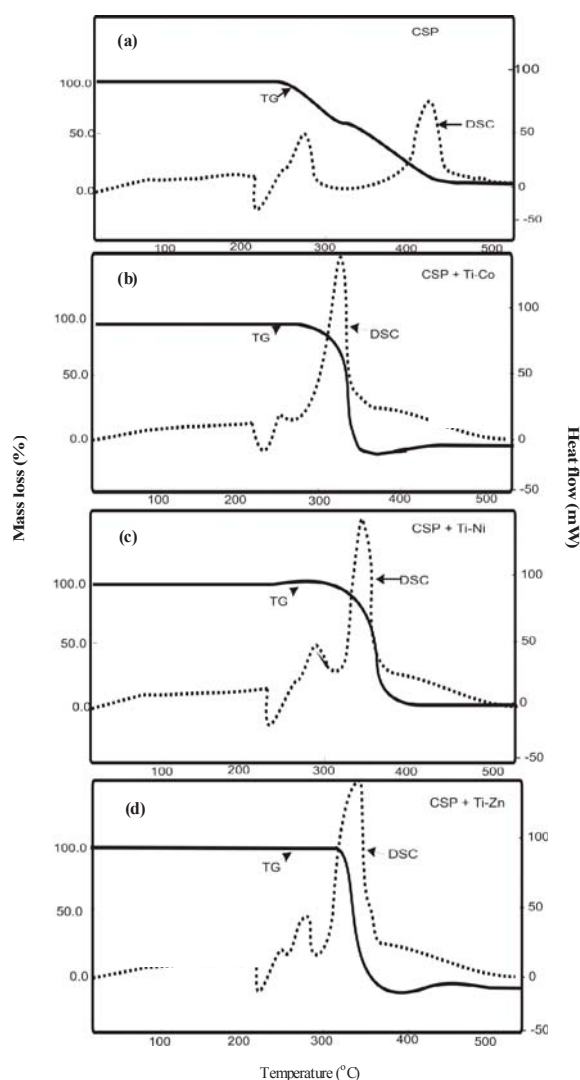
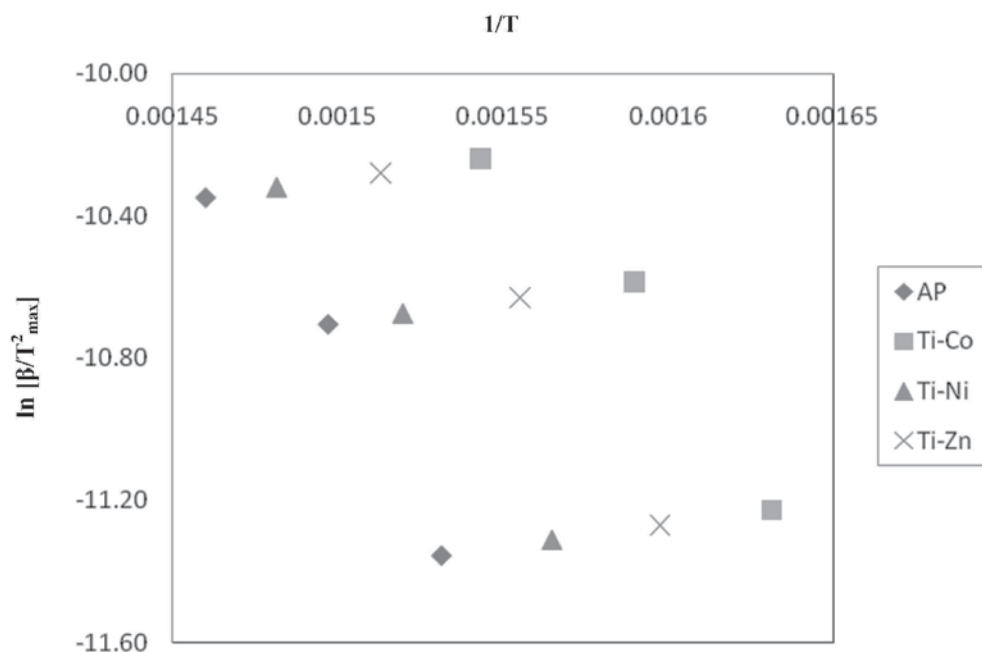


Fig. 3: TG-DSC Thermogram
(a) CSP (b) Ti-Co (c) Ti-Ni (d) Ti-Zn

at much lower temperature, which may be due to the activity of BMNs. Lowering of HTD was also support by DTA.

The mass loss was accelerated when BMNs were used as catalysts (1 wt.-%) for CSPs. The mass loss might be enhanced on account of the acceleration of any decomposition of the HTPB, AP, and HTPB/AP. The result shows that the rate of polymer decomposition is enhanced when catalysts are added. Perhaps oxidative degradation of HTPB is increased by catalysts as it has been pointed out in earlier work [16].

Fig. 4: Plot $\ln(\beta / T^2_{max})$ vs $1/T$

In CSPs; AP particles first decompose in the sub-surface region to form perchloric acid (HClO_4), and the HTPB binder decomposes to produce fuel in the form of hydrocarbon fragments and hydrogen. HClO_4 decomposes further to form smaller oxidizing species. These decomposed gases consisting of fuel and oxidizer components mix together to form a diffusion flame above the propellant-burning surface. The flame structure, however, is more complex as there are individual premixed monopropellant flames from AP and partially mixed flames from HTPB, in addition to the diffusion flame from their decomposition products. The luminous flame is attached to the burning surface and there is no dark zone as seen in double-base propellants [17, 18]. The combustion of AP/HTPB composite propellant involves an array of intricate physiochemical processes including: (1) conductive preheating, decomposition, and phase transition in the condensed phase; and (2) multi-stage reactions in the gas phase [19].

CSPs also ignited with noise and flame at sudden high temperature. Activation energy calculation shows that activation energy for ignition of CSPs lowered by the nano-alloys. Summarizing these results, it may be inferred that nano-alloys can be used as catalyst for AP and CSPs.

CONCLUSIONS

BMNs were prepared by hydrazine reduction method and used as catalysts in the thermolysis of AP and CSPs. The burning rate was found to be enhanced with BMNs. TG-DSC studies and activation energy values demonstrated that HTD of AP is enhancing enormously by these nano-catalysts.

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