Thermal Analysis of Electrically Controlled Solid Propellant with Different Metal Additives

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1 Introduction

Electrically Controlled Solid Propellants (ECSPs) are a special class of propellants that are ignited only when an external electric power source is applied. This pyrotechnic behavior of ECSPs makes them ideal for use in space applications as they can be used to control the attitude of a satellite by utilizing ECSPs in micro thrusters, gas generator systems and long-range rocket motors. The ability to start and stop the combustion at will allows for multiple impulse bits and adjustable burning rate, making ECSPs highly stable, controllable and versatile for future rocket motor design. Furthermore, the ability to adjust the electrical power supply to the ECSP allows for a wide range of operating frequencies and allows to control and adjust the combustion rate, making them ideal for use in rocket motors that need to have a stable and controllable thrust. ECSPs have a high potential for future use in multiple applications such as satellite propulsion, space debris removal, and even for interplanetary missions. They could also be used for future high-performance rocket engines with controllable thrust and high stability. This paper discusses the research on ECSP and focuses on understanding the physio-chemical mechanism of ECSP burning and thermal behavior when different metal additives are added. Specifically, the paper looks at the effects of adding aluminum (Al), magnesium (Mg), and titanium (Ti) to the baseline ECSP composition, which consists of lithium perchlorate (LP) as the oxidizer and polyvinyl alcohol (PVA) as the binder.

Adding different metals to an ECSP combustion can affect the thermal stability of the combustion. Different metals can have varying effects on the ignition characteristics and reactivity of the propellant, which can impact the overall stability and efficiency of the combustion process. Thermal analysis using techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) can provide valuable information about the thermal stability and mass loss of ECSPs with different metal additives. The results of these analyses can reveal how the metal additives affect the decomposition of the ECSPs and at what temperature range the decomposition occurs. The results of these analysis shows that the lithium perchlorate-polyvinyl alcohol based baseline composition is not suitable for accommodating all metal additives, and the burning of the ECSP stops when magnesium is added to the baseline. This would suggest that the baseline composition needs to be modified in order to accommodate different metal additives and optimize the thermal stability and performance of the ECSP.

Sawka et al. [1] synthesized a hydroxyl ammonium nitrate (HAN) based composition and demonstrated its utility as an ECSP (electrically controlled solid propellant) for micro to macro propulsion technology by performing experiments up to 6.8 MPa in a closed bomb setup. The experiments showed that after 1.36 MPa the ECSP burning becomes self-sustaining, which is a drawback of this propellant. The drawback of the self-sustaining combustion at high pressure needs to

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be addressed in future research. Bao et al. [2] studied the effect of graphite as an additive to the HAN based ECSP and found that the introduction of carbon increases the thermal conductivity of the propellant, but at the expense of reducing the adiabatic flame temperature. Gnanaprakash et al. [3] have adopted a similar baseline composition as He et al. [4], which is a lithium perchlorate-polyvinyl alcohol (LP/PVA) based ECSP, but with a different metal additive, Tungsten (W). This research supports the idea that different metal additives can have a significant effect on the thermal stability of ECSPs.

He et al. [4] performed experiments on a lithium perchlorate (LP) and polyvinyl alcohol (PVA) based ECSP with aluminium as a metal additive, in the pressure range of 0.1 – 5 MPa, with aluminium powder below 20% in the composition. They found that the LP based ECSP had higher thermal stability and high electrical control relative to HAN based compositions which are hygroscopic in nature. Glascock et al. [5, 6] formulated an Electrically Controlled Solid Propellant (ECSP) based on Hydroxyl Ammonium Nitrate (HAN) and Polyvinyl Alcohol (PVA) and studied the ablation of the ECSP due to arc discharge. They found that the ECSP had a higher specific ablation per pulse, but that the HAN component of the ECSP was hygroscopic, which caused the surface layer to be rapidly ablated and decreased the average specific impulse. The formation of the liquid decomposition layer which when spread to the anode accelerates the decomposition of the perchlorate ions. Baird et al. [7] reported that the electrode area ratio affects the preferential burning of an electrically controlled solid propellant (HAN + PVA based). They found that combustion always occurs at the smaller electrode, regardless of the polarity of the electrodes. This suggests that the electrode area ratio plays a significant role in determining the burning behavior of this type of propellant.

This paper aims to investigate the effect of various metal additives on combustion when blended with the baseline composition of an Electrically controlled solid propellant (ECSP). This study also includes the thermal analysis of these metal-additive composition blends. It is evident that not much research has been done in this area and this study is an attempt to understand the effect of metal additives on ECSP, as no such studies have been reported in the past.

2 Experimental Section

2.1 Propellant preparation

The main ingredients of the Electrically controlled solid propellant (ECSP) samples used in the study are: Lithium perchlorate (Alfa Aesar Ltd.) with a purity of 99.0% as an oxidizer. Polyvinyl alcohol (Sigma-Aldrich Ltd.) with a molecular weight of 146,000–186,000 and a degree of hydrolysis of > 99.0% as binder/fuel. Boric acid (H3BO3) as a cross-linking agent. As metal fuel additives, the study uses: Magnesium (US Research Nanomaterials Inc.) with a particle size of 10 μm. Titanium (US Research Nanomaterials Inc.) with a particle size of 800 nm. Aluminium (US Research Nanomaterials) with a particle size of 10 μm. Different compositions of Electrically controlled solid propellant (ECSP) were synthesized to understand the effect of different metal additive. The weight ratio of lithium perchlorate (LP) and water was maintained to be 1:1.85, which is slightly greater than the solubility limit. Three different compositions were created, each with a different metal additive: The first composition contained 5% Mg, the second composition contained 1% Ti and the third composition contained 1% Al. The ingredients were mixed using a planetary centrifugal mixer (Thinky ARE-310, Japan) for a total of 45 minutes to homogenize the ingredients after LP and PVA were dissolved in water. The different compositions and their metal additive content are shown in Table 1 of the study.

Table 1: ECSP composition.

Ingredients	M0 (mass in g) Baseline	M1 (aluminium based, 1%)	M1 (Titanium based, 1%)	M5 (Magnesium based, 5%)

Distilled water	5.388	5.3228	5.3228	5.063
LP	2.912	2.8772	2.8772	2.737
PVA	1.0	1.0	1.0	1.0
Metal	0.0	0.1	0.1	0.5
Glycerol	0.5	0.5	0.5	0.5
Boric acid	0.2	0.2	0.2	0.2

2.2 Characterization methods

To understand the thermal behavior of the different compositions of Electrically controlled solid propellant (ECSP), thermal analysis of the samples was conducted using Differential scanning calorimetry (DSC 3+, Mettler Toledo) and Thermogravimetry (TGA 2, Mettler Toledo) techniques at different heating rates. These techniques were used to characterize the ECSP samples and identify any thermal properties and behavior that might be affected by the different metal additives. For the Differential scanning calorimetry (DSC) experiments, small samples of the ECSP (around 1mg) were placed in a 40 µl Al crucible, sealed with a perforated covering and the standard nitrogen flow of 40 ml/min was applied. The samples were then heated at a range of temperatures from 30 ℃ to 600 ℃, and the thermal properties and behavior of the samples were observed and analyzed. To investigate the decomposition of the ECSP samples, the TGA experiments were conducted using four different heating rates: 5 ℃/min, 10 ℃/min, 15 °C/min and 20 °C/min. The samples were placed in a 40 µl Al crucible and heated between 35 ℃ to 600 ℃. The crucible was left unsealed and around 1mg of the sample was used for the analysis. The thermal properties and behavior of the samples were observed and analyzed. The experiments were conducted following the International Confederation for Thermal Analysis and Calorimetry Kinetics Committee's recommendations to ensure the validity of the results. Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) analysis was also performed to observe the surface morphology and elemental composition of the ECSP samples. A field emission scanning electron microscope (FE-SEM, ZEISS GeminiSEM 560, ZEISS, Germany) with a resolution of 0.5 nm at 15 kV was used. The GeminiSEM 560 is equipped with a Gemini column that features Schottky type field emission and in-column beam deceleration design, allowing for high-resolution imaging and surface morphology observation at low acceleration voltages without stage bias. Additionally, the 8.5mm analytical working distance enables excellent EDS signal acquisition and good mapping results.

3 Results and Discussion

3.1 Surface morphology

The surface morphology and elemental composition of the three metallized ECSP samples were studied using SEM and EDS techniques. The SEM-EDS of the magnesium-based ECSP is shown in Figure 1. Based on the physical appearance of the slurry formed after mixing the propellant ingredients, it was found that the mixture was homogeneous without any air bubbles, blow holes or voids, indicating that the mixing process was successful. Once the curing is done, the samples protrusion and irregularity were the results of the evaporation of the water content in the ECSP sample. SEM images shows the homogeneity obtained while synthesizing the sample and the EDS mapping of the residue from the thermal analysis experiments shows the elemental mapping corresponding to the ECSP sample.

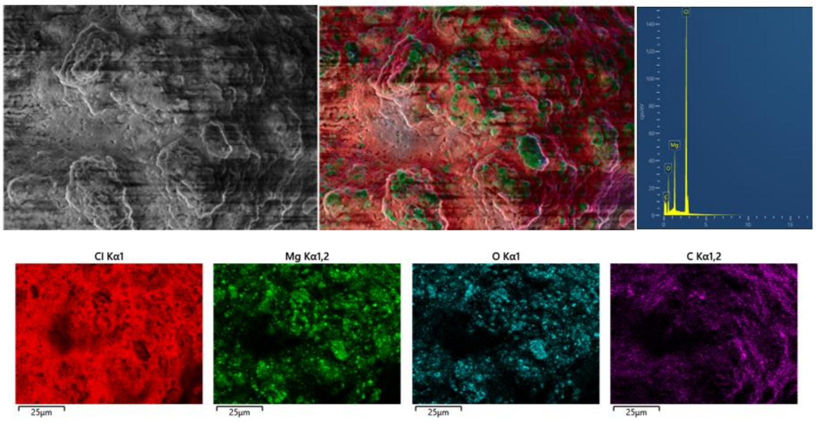

Figure 1: SEM image and EDS mapping of residues from thermal experiments for Mg based composition.

The EDS mapping results indicate that the metal additive is homogenously distributed throughout the ECSP sample, as the elemental mapping of Mg is observed throughout the sample. The presence of C, O, and Cl in the EDS mapping confirms the presence of PVA, LP, and H3BO3 in the sample, respectively. The EDS mapping results provide a strong indication that the synthesized ECSP samples are of good quality and the metal additive is well blended with the ECSP composition.

3.2 Thermal analysis

DSC and TGA experiments were performed on three different metallized ECSP samples (Mg, Al, Ti) to investigate their thermal stability and heat of reaction. The DSC, TGA and dTG curves for Mg, Al and Ti based ECSP samples at heating rates 15 ℃/min are shown in Fig.2, Fig.3, and Fig.4. The DSC curves of all the samples show an endothermic peak at around 98 ℃ and the decomposition temperature of the Al and Ti based samples falls in the range of 280-440 ℃ at a heating rate of 5 ℃/min, 10 ℃/min, 15 ℃/min and 20 ℃/min. But the decomposition of the magnesium based ECSP initiates at the higher temperature as compare to aluminium and titanium based ECSP samples. The TGA experiments revealed a relative mass loss of up to 10% during the first endothermic peak, which is attributed to the evaporation of water in the samples. Additionally, the SEM-EDS analysis showed the surface morphology and elemental mapping of the samples, with the presence of C, O, Cl, and Mg (the presence of Cl indicating the existence of LiCl in the composition). However, Lithium cannot be identified from the EDS analysis.

The endothermic peaks at heating rates of 20 ℃/min are more pronounces as compared to the DCS curves of all the ECSP samples at the heating rate of 10 ℃/min. In both the heating rates of 10 ℃/min and 20 ℃/min, it is seen that the decomposition temperature of the aluminium and titanium based ECSP samples fall in the temperature range of 280 ℃ to 380 ℃ whereas at 5 ℃/min and 15 ℃/min heating rates the decomposition temperature range is widening. At heating rate of 5 ℃/min, it is noticed that the second exothermic peak for the titanium based ECSP is observed above 400 ℃. Similar observation is not noticed for the titanium based ECSP at the heating rate of 20 ℃/min. The relative mass loss for all the ECSP compositions, at different heating rates during the first endothermic peak at the DSC curve, is up to 10 %, and this mass loss is due to the evaporation of the water in all the ECSP samples considered in this study. The decomposition of the aluminium and titanium based ECSP initiates at around 280 ℃, exothermic peaks can be seen between the temperature range of 280 ℃ to 440 ℃. A significant amount of mass loss happens to the aluminium based ECSP as compare to the titanium based ECSP. For aluminium based ECSP the mass loss after the decomposition is around 80 % and for titanium based ECSP the mass loss after the decomposition is around 50 %. This means that the thermal stability of the aluminium based ECSP is less relative to the titanium based ECSP. Decomposition of the magnesium based ECSP starts at the temperature around 380 ℃ at the heating rate of 5 ℃/min and it starts at around 400 ℃ for the heating rate of 15 ℃/min.

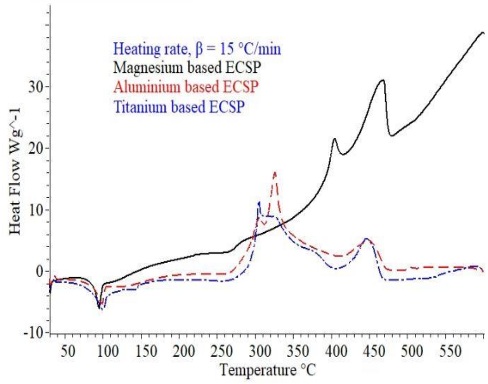

Figure 2: DSC curve for Mg, Al and Ti based ECSP at heating rate of 15 ℃/min

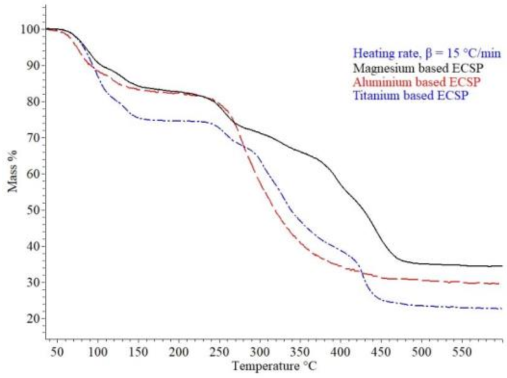

Figure 3: TGA curve for Mg, Al and Ti based ECSP at heating rate of 15 ℃/min.

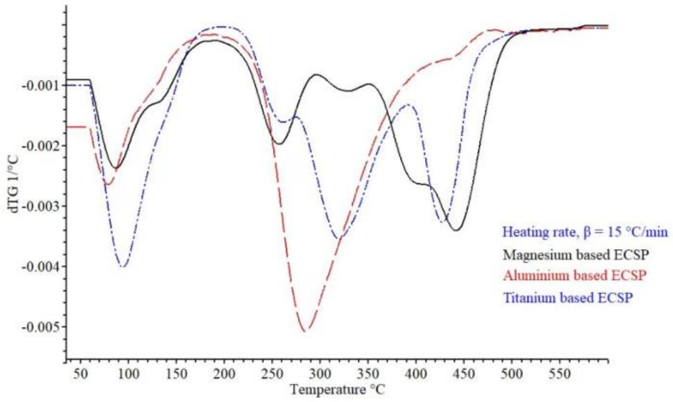

Figure 4: dTG curve for Mg, Al and Ti based ECSP at heating rate of 15 ℃/min.

It is noticed that the thermal stability of the magnesium based ECSP is higher than any other composition considered in this study. Table 2 lists the heat of reaction and the mass loss during the thermal analysis of the various ECSP samples considered in this study.

Table 2: Heat of reaction and mass loss for different ECSP samples.

Samples	Average heat of reaction (J/g)	Average mass loss (%)	Heating rate (℃/min)	Decomposition temperature (℃)
Mg (5%)_ECSP	595 & 1877.91	25 & 55	5	382 & 451
Al (1%)_ ECSP	1305 & 723	25 & 45	5	312 & 431
Ti (1%)_ ECSP	1460 & 1049	25 & 65	5	305 & 405
Mg (5%)_ECSP	1862	55 & 65	10	389 & 462
Al (1%)_ ECSP	2552.17	22	10	275
Ti (1%)_ ECSP	1860 & 892	22 & 61	10	303 & 431
Mg (5%)_ECSP	184 & 898	30 & 65	15	403 & 468
Al (1%)_ ECSP	2319 & 426	30 & 65	15	326 & 451
Ti (1%)_ ECSP	1878 &576	25 & 75	15	305 & 447

Mg (5%)_ECSP	1862.9	55 & 65	20	389 & 462
Al (1%)_ ECSP	2552.17	22	20	275
Ti (1%)_ ECSP	1860.89	22	20	303

Table 2 compares the heat of reaction, % mass loss and decomposition temperature for the two different heating rates are considered in this study. The decomposition temperature for the magnesium based ECSP is always above 400 ℃. When compared to previous ECSP samples with different metal additions, it has been shown that the thermal stability of the magnesium-based ECSP is significantly more prominent. The decomposition of the magnesium-based ECSP sample takes place between 400 ℃ and 500 ℃, whereas the decomposition of the titanium and aluminum-based ECSP samples takes place between 300 ℃ and 400 ℃. Thermal analysis and chemical kinetic analysis shows that the peak of the reaction rate shifts towards higher temperature at high heating rates.

4 Conclusion

In conclusion, the study investigates the effect of various metal additives on combustion when blended with the baseline composition of the Electrically Controlled Solid Propellant (ECSP). Different compositions of ECSP were synthesized using lithium perchlorate, polyvinyl alcohol, boric acid and metal additives such as magnesium, titanium, and aluminum. Thermal analysis using DSC and TGA were performed to characterize the ECSP samples at different heating rates, and SEM-EDS analysis was used to observe the surface morphology and elemental mapping of the ECSP samples. The results of the study provide insights into the behavior of the ECSP samples with different metal additives and can be used to improve the performance of ECSP in propulsion applications.

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