CHARACTERIZATION OF THE ALUMINUM/POTASSIUM CHLORATE MIXTURES BY SIMULTANEOUS TG-DTA

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Thermogravimetry (TG) and differential thermal analysis (DTA) in the non-isothermal mode have been used to examine the thermal behaviour of the micron sized aluminum (Al) powder/potassium chlorate pyrotechnic systems in air, in relation to the behaviour of the individual constituents. The effects of different parameters of Al powder, such as particle size and its content in the mixtures, on their thermal property were investigated. The results showed that, the reactivity of Al powder in air increases as the particle size decreases. Also, it was found that neat Al with 5 μm particle sizes (Al_5) has a fusion temperature of about 647°C, that for 18 μm powder (Al_{18}) is 660°C. Pure potassium chlorate has a fusion temperature around 356°C and decomposes at 472°C. DTA curves for $Al_5/KClO_3$ (30:70) mixture showed a maximum peak temperature for the ignition of mixture at 485°C. Also, by increasing the particle size of Al powder, the ignition temperature of the mixture increased. On the other hand, the oxidation temperature increased by enhancing the Al content of the mixtures. In this particular study, we observed that the width of reaction peak for the mixtures corresponds to their Al contents of samples.

Keywords: *aluminum powder, ignition temperature, particle size effect, potassium chlorate, pyrotechnic, thermal behaviour*

Introduction

The decrease in the size of energetic materials, e.g., metal fuels, oxidizers and explosives, leads to an increase of the reaction surface area, which considerably enhances the combustion rate of propellant compositions and detonation properties of explosives. The crystal grid defects considerably accelerate the process of the thermal decomposition of energetic materials [1–3]. One of the most important types of defects – dislocations – in a great extent defines the mechanical and physical properties of crystalline materials. The chemical reactions on dislocations proceed much faster than on an ideal crystal. Very fine crystalline materials are known of having a high defect concentration, which is along with the large surface area, the reason to expect the higher chemical activity of very fine materials in comparison to the conventional compounds.

Potassium chlorate and potassium perchlorate have been the main oxidizer in many compositions of propellants and pyrotechnics [4–8]. Although they gives virtually smokeless products of combustion, their use in solid pyrotechnics systems have been interested because of their mild phase transition involving a volume change in low temperature and their fast ignitability.

Very fine Al powder possess unique thermal behaviour, which renders it useful as a fuel in both propellant and explosive formulations. It also has potential applications in pyrotechnic delays, flares and heat generating devices [9–12]. Propellants containing fine powders of Al have considerably enhanced burning rates over those are free of Al powder [13]. This paper presents the results of study on the potassium chlorate/Al powder mixtures using simultaneous thermogravimetry-differential thermal analysis (TG/DTA). The aim of this study was investigation of the effect of Al content and its particle size on the thermal behavior of different compositions of Al and potassium chlorate. Thermal behaviour of neat micro-sized Al and its composition with explosives have been reported previously [14, 15], but to the best our knowledge nothing has been published on the thermal behaviour of Al+potassium chlorate.

Ignition or initiation refers to the point during a chemical reaction at which the rate of heat generation exceeds the required input to sustain the reaction, that is the point at which the reaction becomes self-sustaining. The temperature at which this occurs depends on many variables such as sample mass, geometry, atmosphere and heating rate, so that in most cases it is difficult to measure precisely [16, 17]. In this study as many of these variables as possible were held constant in order to facilitate comparisons that reflect on the particle size and content of Al in the interested mixtures.

Experimental

Materials

Potassium chlorate (mesh 300) was purchased from Merck (Tehran-Iran). Neat Al powders 5 μm (Al_5)

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Table 1 Summary of tested sample's compositions and TG/ DTA results

Sample No.	Component	Composition	Transition temperature/°C		
			fusion	decomposition	T^*
1	Al_5	100	647	–	484–603 (increase)
2	Al_{18}	100	660	–	490–610 (increase)
3	$KClO_3$	100	356	472	472–500 (decrease)
4	$Al_5/KClO_3$	30/70	361	485	485–550 (decrease)
5	$Al_5/KClO_3$	50/50	367	493	493–580 (decrease)
6	$Al_{18}/KClO_3$	30/70	366	535	535–575 (decrease)
7	$Al_{18}/KClO_3$	50/50	372	550	550–600 (decrease)

T^* is the temperature when there is a variation in the sample's mass

and 18 μm (Al_{18}) particles sizes were prepared from metals laboratory of Malek Ashtar University of Technology. Four $Al/KClO_3$ mixtures, as well as pure potassium chlorate, Al_5 and Al_{18} were examined. Table 1 summarizes the tested samples compositions. Before testing, all samples were stored in a vacuum oven at 65°C for at least three hours. The mixtures were prepared by well mixing of fine Al powder and potassium chlorate powder.

Procedure

A thermobalance (Stanton, model TR-01, sensitivity 0.1 mg) with a differential thermal analysis attachment (STA 1500) was used for TG/DTA studies of pyrotechnic mixtures. Approximately, 4.0 mg of sample and reference (Pt foil) were placed in alumina pans and heated 10ºC min^{-1} from 30 to 800ºC. In this study, the flow rate of purge gas (air) was 10ºC min^{-1} at 1 bar. TG mass, DTA baseline and temperature calibrations were performed prior to the experiments [18].

Results and discussion

Thermal behaviors of the individual components

Aluminum powders

Al_5 and Al_{18} were examined in air using simultaneous TG/DTA to assess its oxidation characteristics. The TG/DTA results for the two different Al powders in air are shown in Fig. 1. The powders exhibit an exothermic peak, which is below the melting point of Al. The first mass gain for Al_{18}, Δm_1=12.5%, was observed at the temperature interval 490–610ºC. However, this range (Δm_1=15.4%) for Al_5 was 484–603ºC. It means that Al_5 has a higher reactivity rather than Al_{18} powder. Also, it has a lower melting point (647ºC) rather than Al_{18} (~660ºC).

Potassium chlorate

The DTA and TG curves for pure potassium chlorate are shown in Fig. 2. No thermal event observed prior to the melting point near 356ºC. At this point (356ºC), potassium chlorate undergoes a sharp endothermic phenomenon containing melting, without any change in the mass of sample. As shown in the DTA curve in Fig. 2, there is a long temperature interval of 115ºC between the melting (356ºC) and the first decomposition step (472ºC) of potassium chlorate. On the other hand, TG curve for potassium chlorate showed considerable decreasing in the sample mass (approximately 40%) in temperature range between 472–500ºC. Therefore, this behavior would suggest that, pure potassium chlorate is kinetically stable at its melting point [19]. After the complete decomposition of the sample, oxygen and potassium chloride produced [7, 20]. This statement agrees with TG curve of this sample in Fig. 2.

Binary mixtures

Al_5/potassium chlorate mixtures

The TG and DTA curves for $Al_5/KClO_3$ mixture (30:70) are shown in Fig. 3a. The DTA curve showed an endothermic peak maximum at about 361ºC, which corresponded well with the temperature of fusion of the potassium chloride eutectic. On the other hand, a sharp exothermic occurs near 530ºC and a mild reduction in the mass of sample that it corresponds to the reaction of Al powder with potassium chlorate according following equation:

$$2Al+KClO_3 \rightarrow Al_2O_3+KCl$$

Figure 3b shows the TG/DTA results for $Al_5/KClO_3$ with mass ratio of 50:50. An endotherm was observed at an onset temperature of 367ºC which is due to the fusion of potassium chlorate. Also, an exotherm with a limited decreasing in the mass was occurred at maximum peak temperature 543ºC, which

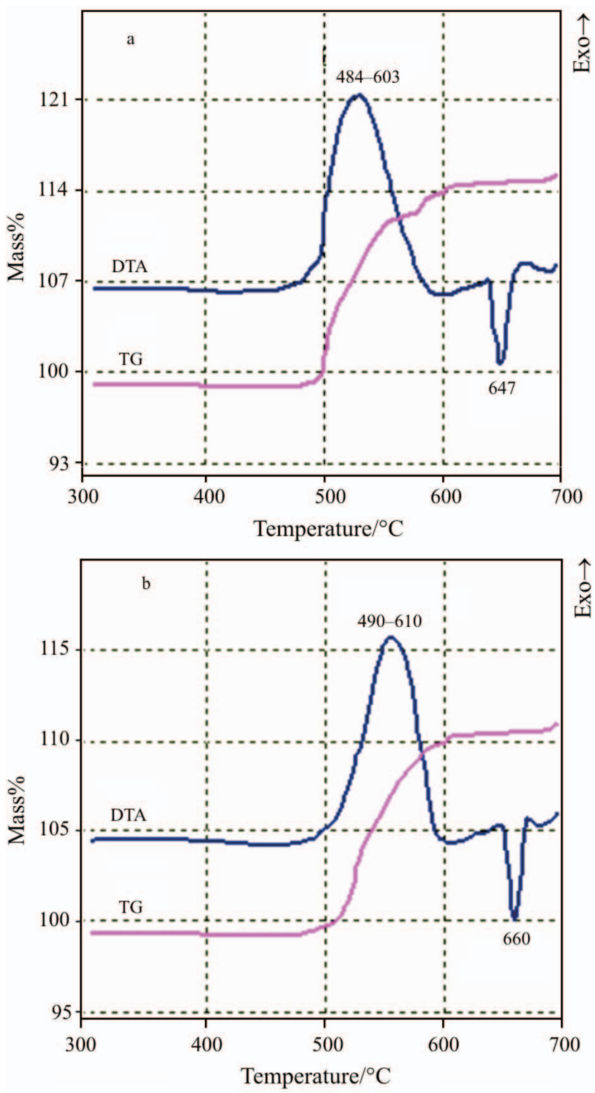

Fig. 1 TG and DTA curves for neat Al powder a – Al_5 and b – Al_{18} (sample mass 4.0 mg; heating rate 10°C min^{-1}; air atmosphere)

corresponds with the reaction between Al and potassium chlorate. As the results showed that the decomposition temperature of these mixture varied as a function of the amount of Al contained in the sample. As shown in Table 1 and Fig. 3, by using a higher content of the Al powder in the mixture, the decomposition temperature of the mixture increases.

Al_{18}/potassium chlorate mixture

TG/ DTA data for $Al_{18}/KClO_3$ mixtures are presented in Fig. 4. As can be seen in Fig. 4a, there are two thermal transitions, one is endothermic and another is exothermic. The endotherm with maximum 366ºC is in good agreement with the fusion point of pure $KClO_3$. Another is exothermic peak on the DTA curve with its maximum at 565ºC, where the stage of mass losses has

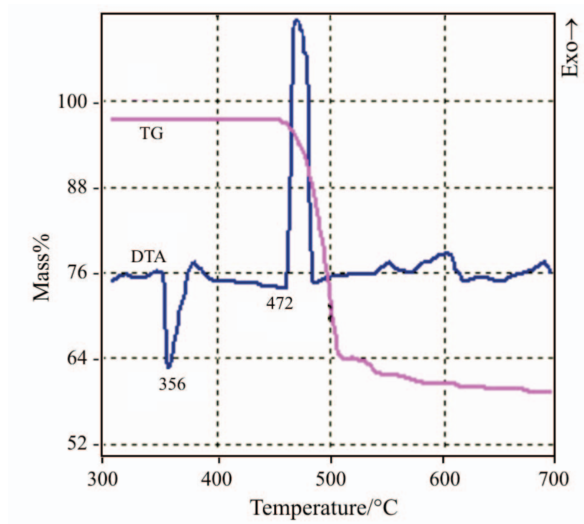

Fig. 2 TG and DTA curves for potassium chlorate (sample mass 4.0 mg; heating rate 10°C min^{-1}; air atmosphere and potassium chlorate with mesh 300)

been observed. Consequently, it can be related to the reaction between Al powder and potassium chlorate.

Figure 4b shows the TG and DTA curves for $Al_{18}/KClO_3$ (50:50) mixture. As seen in this figure, the potassium chlorate has fusion temperature of 372ºC. There is also a complicated exotherm at about 580ºC with a fall in the mass of sample corresponding to the Al/potassium chlorate reaction. These results showed that the ignition temperature of these mixtures increased when higher content of Al powder were used.

Comparison of mixtures

As can be seen from the Table 1 and Figs 3 and 4, the particle size of Al powder and the content of Al in the mixture could affect the fusion temperature of potassium chlorate. The larger particle size of Al and the more content of this powder in the mixture increase the fusion temperature of potassium chlorate. Also, increased Al content of the mixtures, will enhance the ignition temperature of the mixture. On the other hand, the width of ignition peak for the combustion reaction of Al+potassium chlorate varies over a wide range depending on the Al content of the mixture. By increasing the amount of Al in the mixture (from 30 to 50%), the wide of ignition reaction peak will increase. This phenomenon was observed, because increasing the amount of Al powder in the mixture will increase the amount of its product (Al_2O_3) in the reaction. Due to the higher heat capacity of Al_2O_3 in comparison with other components presented in the reaction, the heat in the cell area will be absorbed by Al_2O_3. This process could produce wide peak in comparison with other mixtures that have a lower amount of Al_2O_3 in their products.

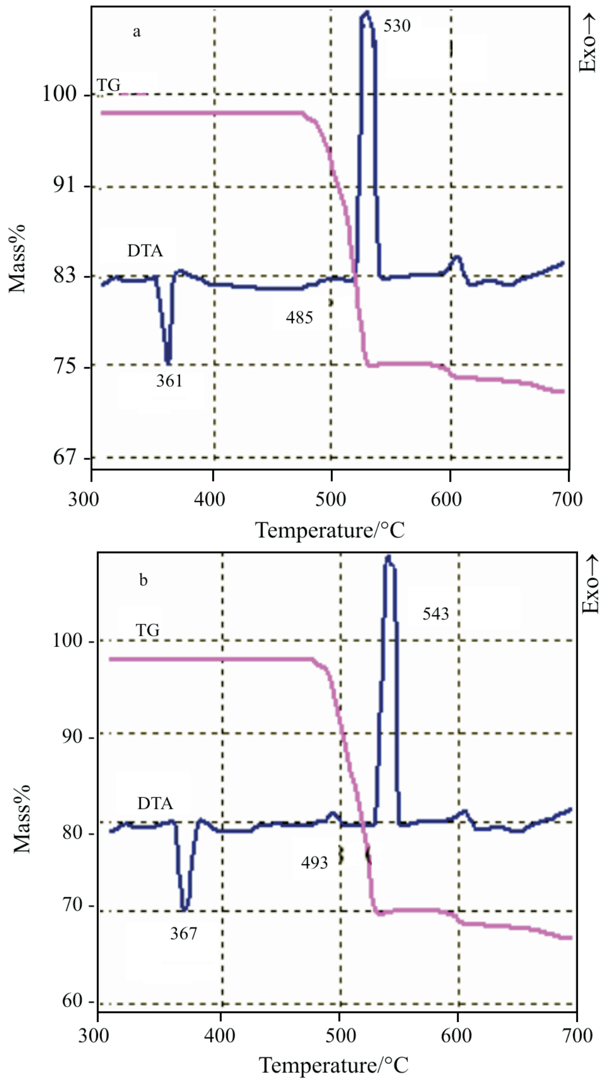

Fig. 3 TG and DTA curves for mixture of Al_5 and potassium chlorate with mass ratio a – 30:70 and b – 50:50 (sample mass 4.0 mg; heating rate 10°C min^{-1}; air atmosphere and potassium chlorate with mesh 300)

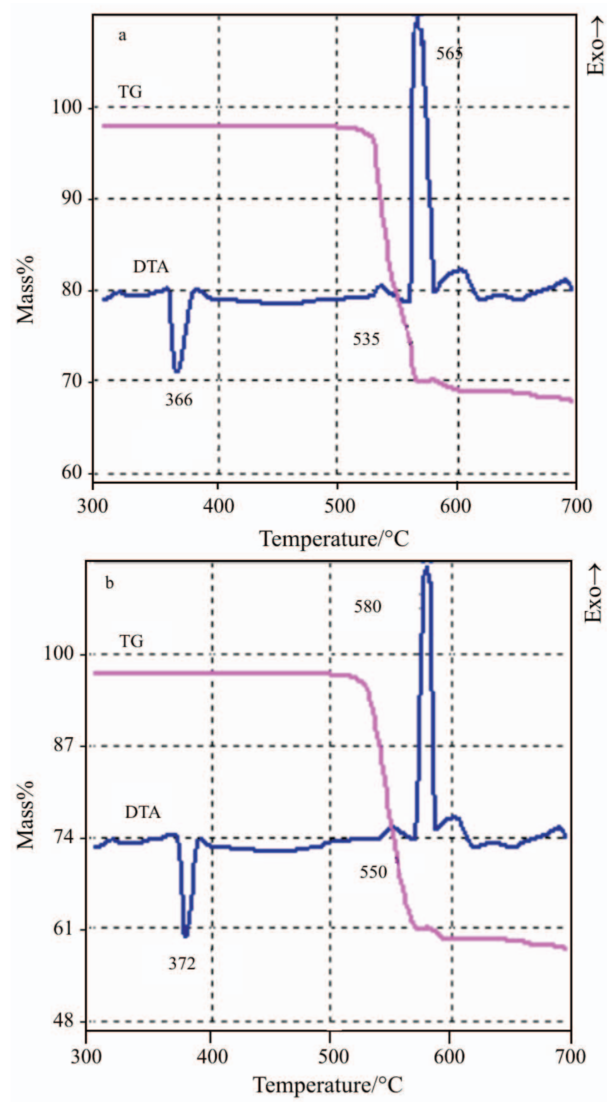

Fig. 4 TG and DTA curves for mixture of Al_{18} and potassium chlorate with mass ratio a – 30:70 and b – 50:50 (sample mass 4.0 mg; heating rate 10°C min^{-1}; air atmosphere and potassium chlorate with mesh 300)

Conclusions

In this study, the effects of different parameters, such as Al particle size and Al content, on the thermal behaviour of Al+potassium chlorate mixtures were investigated. The results obtained by TG and DTA were used for comparison. The results showed that neat Al powder gain mass in the temperature between 480–610ºC due to the oxidation. Also, it was found that the reactivity of Al powder depends on the particle size. Al_{18} powders are less reactive in the air and also in the mixture than the Al_5. Its lower reactivity may be due to a relatively smaller surface area. On the other hand, the reaction peak width for these mixtures is dependent on the Al content of the samples and by enhancing the Al content of the mixture, the width of this peak will increase.

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