

ENERGY RELEASE IN THE REACTION OF METAL POWDERS WITH FLUORINE CONTAINING POLYMERS

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Abstract

Fluorine and its derivatives have been used as a substitute to oxygen-containing oxidizers in higher performing propellants and other energetic materials. They typically react rapidly with metals or thin oxide layers of the metals to produce metal fluorides, generally in the gaseous state.

Thermal reactions of stoichiometric mixtures of metal ($M=Al, Ti$) -F containing polymers have been studied using thermal analyzers and their energetics are compared with the metals in other halogen element containing oxidizers. The experimental results indicated that thermal reaction becomes more exothermic as the bond strength between $Al-X$ ($X=F, Br, I$) becomes stronger. It was also found that oxidation of metal powders is largely affected by the size of metal powders as well as the nature of existing oxide layer.

Keywords: metal/halogen compounds, pyrotechnics

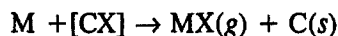
Introduction

The use of fluorine or its derivatives as oxidizers in various propellants and explosives has been recognized for many years [1]. The reaction of fluorine and its derivatives with metals and metal hydrides is of interest in various pyrotechnics including flares, igniters, and incendiaries. Generally, energetic compositions containing fluorine-based oxidizers are used in relatively small, specialized munitions where the higher cost of fluorine containing ingredients can be justified by their unique characteristics.

Metal powders such as aluminum (Al), magnesium (Mg), titanium (Ti), and hafnium (Hf) react exothermically with decomposition products of fluorine containing polymers to produce metal fluorides, generally in the gaseous state yielding comparatively high flame temperature, enthalpy release and energy density. The decomposition temperature and extent of reaction depend, to a great extent, on the size as well as shape of the metal particles [2]. Furthermore, for most metal powders, under normal condition, oxidation is retarded by a thin, but tough oxide film, and reactions with decomposed fluorine compounds are greatly influenced by the quality of oxide layer.

Understanding the complex physicochemical processes that underlie the decomposition of these materials can lead to methods for modifying the propellant and explosive formulations in order to obtain better ignition, combustion, or sensitivity.

In this work, thermal analysis was employed to determine the temperature required to initiate and the extent of the general reaction;



where, M =metal (Al and Ti) and X =F, Br, and I.

Experimental

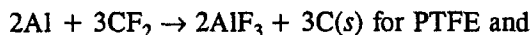
Aluminum (Al, 99.7% purity, $\approx 20 \mu\text{m}$, Valley Metallurgical)/Polytetrafluoroethylene (PTFE, 35 μm and 500 μm) and Al/polychlorotrifluoroethylene (Kel F, M. W. Kellogg) mixtures were prepared as a dry powder mixture by the mortar and pestle method. A sample of PTFE (35 μm)/Al ($\approx 200 \text{ nm}$) was also prepared to observe effects of metal particle size on thermal decomposition behavior of a metal/polymer mixture. Samples of Al/decabromodiphenyl ether (DBDPE) and Al/iodoform were prepared as dry powder mixtures by mixing aluminum in stoichiometric amounts of polymers assuming the formation of aluminum trihalides.

Titanium (Ti, 99.5% purity, $\approx 20 \mu\text{m}$)/PTFE was prepared as a dry powder mixture from stoichiometric amounts of titanium powder and PTFE. In the case of Kel F, the polymers were melted at $\approx 400^\circ\text{C}$ and titanium powders were mixed by stirring.

Thermal analyses of the metal/polymer compounds were performed using the TA 2000 system. The simultaneous differential thermal and thermogravimetric analyses were performed from room temperature to 1000°C at a heating rate of $10^\circ\text{C min}^{-1}$ with a gentle flow of Ar gas ($80 \text{ cm}^3 \text{ min}^{-1}$) using a TA 2600 thermal analyzer.

Results and discussion

Fluorine containing polymers such as PTFE and Kel F decompose largely by depolymerization to the volatile monomer [3]. If a reaction occurred between aluminum and gaseous product of PTFE or Kel F, thermally stable aluminum fluoride would be expected from the following reaction;



However, in the presence of fluorine and oxygen containing compounds, the thermochemical calculations predict AlOF as a major product [2]. The DTA curves (Fig. 1) show melting of PTFE and Kel F at 348°C and complete decomposition at 556°C and 425°C for PTFE and Kel F, respectively. Figure 1 also shows a comparison of thermal response of PTFE with different particle sizes (35 μm vs.

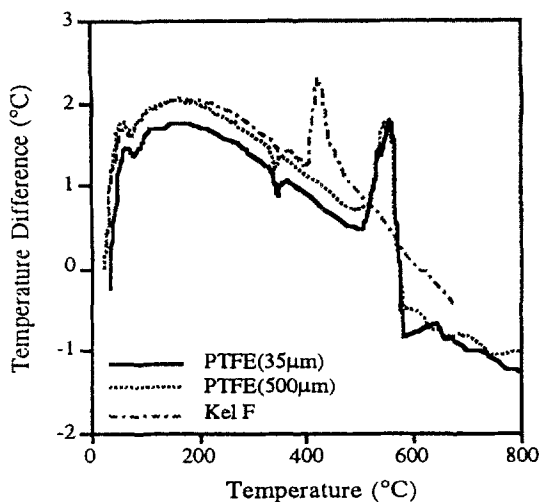


Fig. 1 DTA curves of Kel F and PTFE with different particle sizes

500 μm). It indicates that the particle size differences of the PTFE with approximately same crystallinity ($\approx 60\%$) do not affect thermal behavior. Figure 2 compares the SDT curves of Al/PTFE mixtures with two different particle sizes of Al. Al/PTFE mixture with 20 μm aluminum powder shows a major mass loss ($\approx 65\%$) at $\approx 530^\circ\text{C}$ associated with a small exothermic peak due to the reaction of decomposition product of PTFE with aluminum. However, the oxidation was not associated with a violent exothermic reaction that would be useful for energetic applications. A gradual mass increase after the major mass loss at $\approx 530^\circ\text{C}$ indicates an oxidation of residual aluminum and it continued until 1000°C where heating was

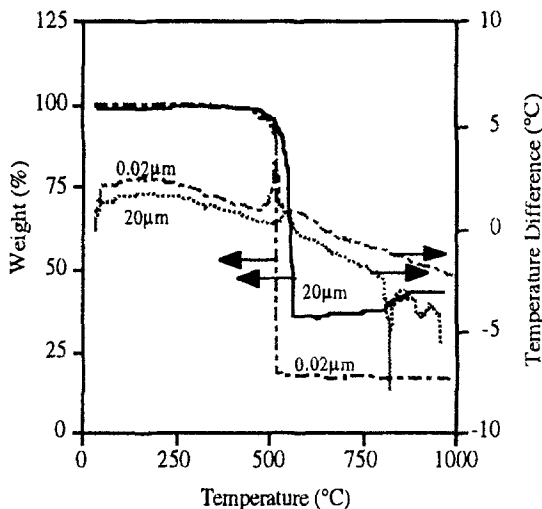


Fig. 2 SDT curves of Al/PTFE mixtures with two different Al particle sizes

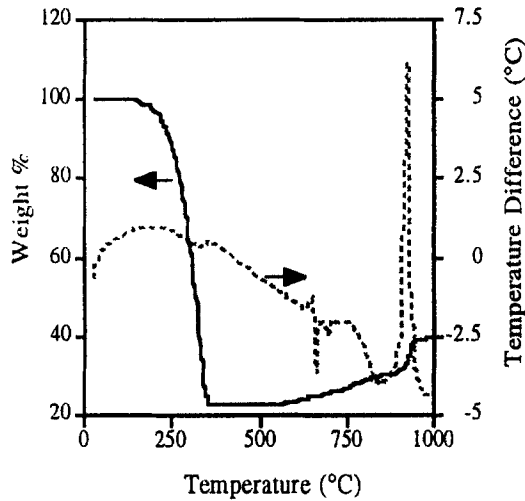


Fig. 3 SDT curves of Al/Kel F

completed yielding $\approx 10\%$ mass gain. The sample with nano size aluminum particles, however, showed a strong exothermic reaction at $\approx 520^\circ\text{C}$ with a major mass loss ($\approx 83\%$). No mass gain after the exothermic reaction implies a complete oxidation of aluminum.

Aluminum mixed with Kel F showed a significant exothermic reaction at 840°C as a threshold temperature after a major mass loss initiated at $\approx 197^\circ\text{C}$ (Fig. 3). An endothermic peak at 661°C indicates a melting of aluminum.

Figure 4 shows the curves of aluminum mixed with decabromodiphenylether. It lost 86% of mass at $\approx 450^\circ\text{C}$ and, unlike aluminum mixed with Kel F, it showed a small and broad exothermic reaction associated with mass gain at $\approx 850^\circ\text{C}$.

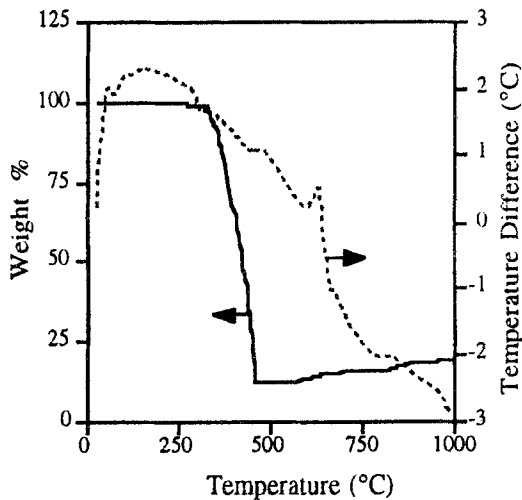


Fig. 4 SDT curves of Al/decabromodiphenylether

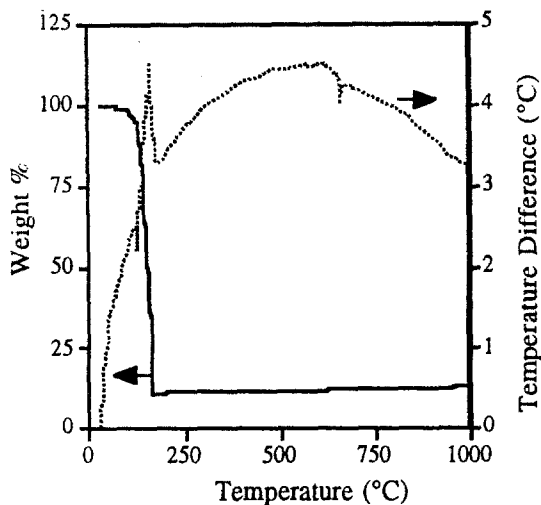


Fig. 5 SDT curves of Al/iodoform

The absence of a strong exothermic reaction in Al/DBDPE, unlike Al/Kel F, is probably due to weak Al-Br bond compared to Al-F.

Aluminum with iodoform showed a single exothermic reaction at 163°C which is due to decomposition of iodoform (Fig. 5). A small endothermic peak at 661°C is due to the melting of aluminum. It was observed that the mixture of Al/iodoform did not show any observable exothermic reaction associated with mass gain of sample. Figure 6 shows DTA curves of Al/Kel F, Al/DBDPE, and Al/iodoform normalized with each sample weight. The figure shows a strong exothermic peak initiated

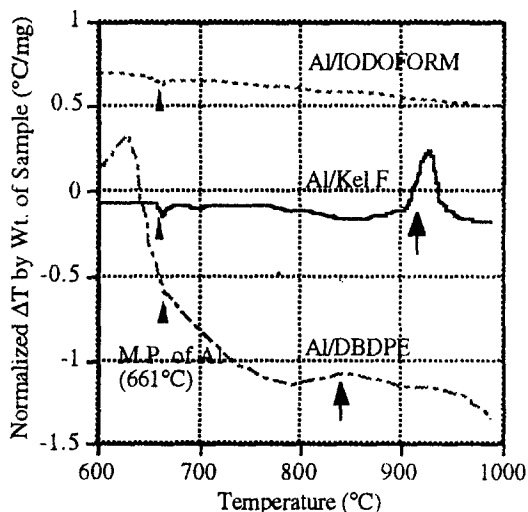


Fig. 6 DTA curves of Al/Kel F, Al/DBDPE, and Al/iodoform normalized with sample mass

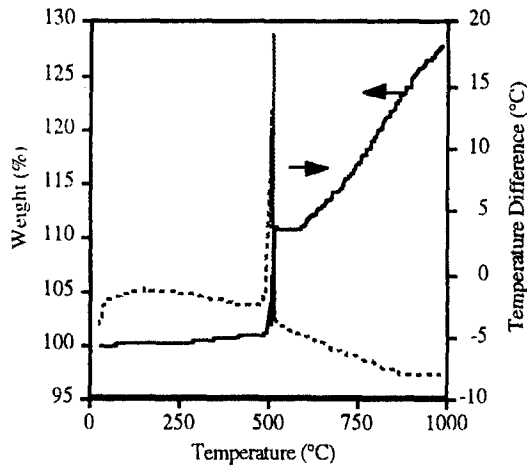


Fig. 7 SDT curves of Ti/PTFE

at 880°C for Al/Kel F and a small exothermic reaction at $\approx 800^\circ\text{C}$ for Al/DBDPE. No evidence of exothermic reaction in Al/iodoform can probably be ascribed to a depletion of oxidizer around aluminum powders due to an early decomposition of iodoform (161°C). Although the desired strong exothermic reactions were not observed from all of the aluminum/polymer mixtures, the results indicated that the reactions became more exothermic as the bond strength between Al-X ($X = \text{F}, \text{Br}, \text{I}$) becomes stronger (i.e., $\text{Al-F} > \text{Al-Br} > \text{Al-I}$).

Figures 7 and 8 compare the DTA and TG curves of titanium mixed with PTFE and Kel F. Unlike aluminum ($\approx 20 \mu\text{m}$)/polymer mixtures, polymer mixtures of titanium showed strong exothermic peaks associated with major mass gain at $\approx 500^\circ\text{C}$ for Ti/PTFE and $\approx 470^\circ\text{C}$ and 630°C for Ti/Kel F. One of the reason for the differ-

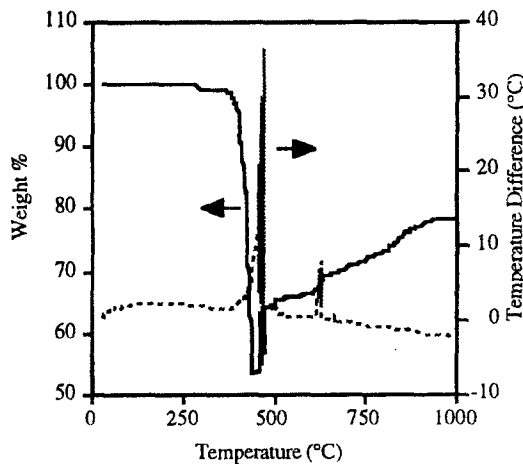


Fig. 8 SDT curves of Ti/Kel F

ence in decomposition behavior of titanium from aluminum is probably due to the differences in the existing oxide layers of the metallic powders. In aluminum, the oxide layer is generally formed from its processing which usually formed by air blowing from the molten aluminum. This protective oxide layer is a thin and tough film that passivates further thermal reactions. Titanium powders, however, are formed by reduction of TiO_2 , and the oxide layer formed during processing has porous structure [4]. Therefore, the diffusion of the decomposed gaseous products of fluorine compounds through the TiO_2 layer is much easier than Al_2O_3 layer on aluminum metal powders.

Conclusions

The thermal analysis revealed an oxidation of metal powders with the presence of decomposed halogen element containing polymers. Although some metal/polymer mixtures did not show a desired exothermic reaction for possible application of the mixtures as an energetic materials, the results indicated that the reactions became more exothermic as the bond strength between $Al-X$ ($X=F, Br, I$) becomes stronger ($F \gg Br > I$). The experimental results also indicated that variation of the particle size and the nature of existing oxide layer on metal surface can significantly affect the extent and initiation temperature for exothermic reaction.

References

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