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Mkhitar Hobosyan

Kh. G. Kirakosyan

S. L. Kharatyan

Karen S. Martirosyan

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Complete List of Authors:	Hobosyan, M.; University of Texas at Brownsville, Physics and Astronomy Kirakosyan, Kh.G.; Institute of Chemical Physics, Kharatyan, S.; Institute of Chemical Physics, Martirosyan, Karen; University of Texas at Brownsville, Physics and Astronomy
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Study of dynamic features of highly energetic reactions by DSC and High-Speed Temperature Scanner (HSTS)

M.A. Hobosyan[1], Kh.G. Kirakosyan[2], S.L. Kharatyan[2,3], K.S. Martirosyan[1*]

[1]University of Texas at Brownsville, Department of Physics and Astronomy, Brownsville, TX 78520, USA
[2]Institute of Chemical Physics NAS RA, Yerevan, 0014, Armenia
[3]Yerevan State University, Yerevan, 0025, Armenia,

ABSTRACT

The dynamic features of Al_2O_3 - polytetrafluoroethylene (PTFE) and Al - PTFE reactions in non-isothermal conditions are presented. The Differential Scanning Calorimetry (DSC) and High-Speed Temperature Scanner (HSTS) were used to characterize the Al_2O_3/Al – PTFE reactions at different heating rates. The study shows that the HSTS instrument can give more information about the reaction mechanism and kinetics than the conventional DSC measurements. In this work we show that high heating rates may reveal exothermic reaction between Al_2O_3 and PTFE that were previously unidentified. The PTFE can potentially remove the oxide layer from aluminum in the initial period of the reaction and increase the direct contact area between oxygen and aluminum, which increases the reaction velocity and improves the energy release abilities of the system.

*E-mail: karen.martirosyan@utb.edu

INTRODUCTION

Aluminum reaction with oxygen, polymers and metal oxides exhibits high enthalpy and has been proposed to use for high-energy storage materials [1]. The size reduction of reactant powders such as aluminum from micro- to nano-size increases the reaction front propagation velocity in some systems by two to three orders of magnitude [2, 3]. The Al - polytetrafluoroethylene (PTFE, Teflon[TM]) reaction has been widely investigated in numerous studies due to the importance of this system as an energetic additive of rocket fuels and pyrotechnics in general [4-6]. However, effective ignition of aluminum is problematic due to the oxide layer that naturally forms on the aluminum surface. The PTFE can potentially remove the oxide layer from aluminum and increase the direct contact area between oxygen and aluminum, which increases the reaction velocity and improves the energy release abilities of the system. Due to self-heating of the system, the reaction rate accelerates exponentially and can lead to explosion. In our knowledge, no investigation was made in high heating rates for the system Al - PTFE, where heating rates are comparable to those in self-ignited reaction mixtures. In this work we attempt to study Al_2O_3 - PTFE and Al - PTFE systems at high heating rate up to 3200 °C/min.

MATERIALS AND METHODS

The chemicals used for this study were Aluminum (99.5 %, 100 nm, Sigma Aldrich), Polytetrafluoroethylene (PTFE, 99.99%, 1 μm, Sigma-Aldrich), Al_2O_3 (Spectroscopic grade, TA instruments), and Argon (99.999%, Airgas Company). The DSC-TGAQ-600 (TA Instrument) was used to test Al_2O_3 - PTFE reactions with linear heating range of 20-150 °C/min, with resolution of mass changes of 0.1 microgram, which gives opportunity to work with very small

amounts of mixtures. The experiments at high heating rate were performed by using a High-Speed Temperature Scanner (HSTS-1, Institute of Chemical Physics, Yerevan, Armenia). The samples (20-50 mg) were placed in Pt-foil (thickness of 50 μm) and heated directly by electrical current following the programmable steps. The heating rate of the sample was controlled by the reaction enthalpy and applied power. The temperature history and applied power were continuously recorded during the process. Heating rate of samples can be varied from 10 to 10.000°C /min with the temperature range of scanning, from room temperature up to 1300 °C. The experiment can be stopped automatically at given time or temperature with subsequent fast cooling of samples (up to 200 °C/s). The instrument can be operated in vacuum, air, and inert gas at P≤1 atm. (static conditions). The custom Microsoft based software with graphical interface has been designed to operate HSTS-1 apparatus.

RESULTS AND DISCUSSION

Thermodynamic analysis

Taking into account the fact that Al particles are always coated with an oxide layer, we studied the possibility of Al_2O_3-PTFE reaction, which can be occurred as the first reaction in Al - PTFE mixture:

$$Al_2O_3 + 1.5/n(C_2F_4)_n = 2AlF_3 + 3CO \qquad (1)$$
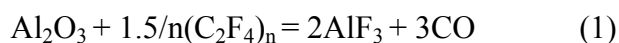
The thermodynamic calculations (THERMO software, ISMAN) of reaction (1) give an adiabatic temperature of T_{ad}=1420K. For this calculation, the enthalpy of 817.5 kJ/mol for Teflon in solid state was used [7].

Differential Scanning Calorimetry of Al_2O_3-PTFE

To study the heating rate impact on the reaction of Al_2O_3 - PTFE, the thermo-calorimetric analysis was guided by 3 different heating rates: 20, 80 and 150 °C/min, in argon flow of 100 ml/min.

DTA/TG curves of Al_2O_3-PTFE mixture at 20 °C/min heating rate are plotted in Figure 1, (left). The DTA result presents a clear endothermic peak at 320 °C, which represents the melting of PTFE with 27.7 J/g of latent heat. At 500 °C starts decomposition of PTFE with endothermic energy utilization of 289 J/g with 59.4 % of a weight loss. According to reaction stoichiometry, 59.5% of the mixture is the PTFE, so this indicates the complete decomposition and removal of PTFE. There is no reaction between Al_2O_3 and PTFE at the heating rate of 20 °C/min.

For the heating rate of 80°C/min, the DTA/TG curves are shown in Figure 1, (center). At 320°C appeared PTFE melting. For the TG curve 53% of a weight loss demonstrates that more than 6% of PTFE remains in system and reacts with Al_2O_3. DTA curve also shows a trend of a broad exothermic peak corresponding to PTFE decomposition.

Finally, at heating rate of 150 °C/min (Figure 1, right) the TG curve shows a well-developed exothermic peak with maximum of 658 °C. Under such high heating rate PTFE melting is unnoticeable. The weight loss at the system is ~44 % so more than 15 % of the PTFE remains in the mixture and reacts with Al_2O_3. The broad exothermic peak is almost covering the endotherm of PTFE decomposition (a little curve at the top of the peak). Therefore it is evident that heating rate affects the reaction mechanism of Al_2O_3 - PTFE. More precisely, at the fast heating rates PTFE remains in the system and reacts with Al_2O_3.
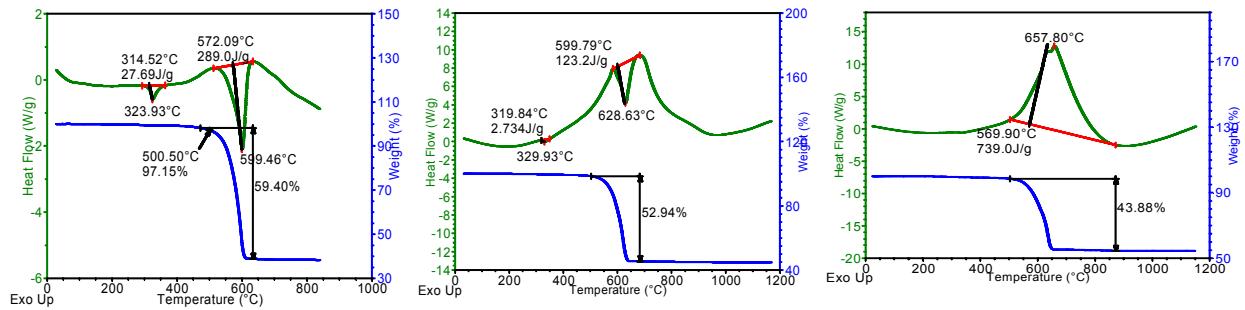
Figure 1. The DTA-DTG curves for Al_2O_3- PTFE at heating rate of (left) 20 ^oC/min; (center) 80 ^oC/min; and (right) 150 ^oC/min in argon.

Activation Energy of Reaction Al_2O_3- PTFE

We estimated the activation energy from the DSC data by using the isoconversional method suggested by Starink [8,9], which was shown in (Ref. [10]) to provide a more accurate value than the Kissinger and Ozawa methods. The Starink method determines the activation energy from the equation:

$$\ln\left(\frac{T^{1.8}}{\beta}\right) = (1.0070 - 1.2 \times 10^{-6} E_a)\frac{E_a}{RT} + const$$

(2)

where E_a is the apparent activation energy (in kJ/mol), β the heating rate in thermal analysis (in K/min), T is the peak temperature of the exothermic curve (in K), and R the universal gas constant. E_a is estimated from the slope of the graph of $\ln(T^{1.8}/\beta)$ vs. 1/T shown in Figure 2. The activation energy for Al_2O_3 – PTFE was estimated to be 265 kJ/mol.
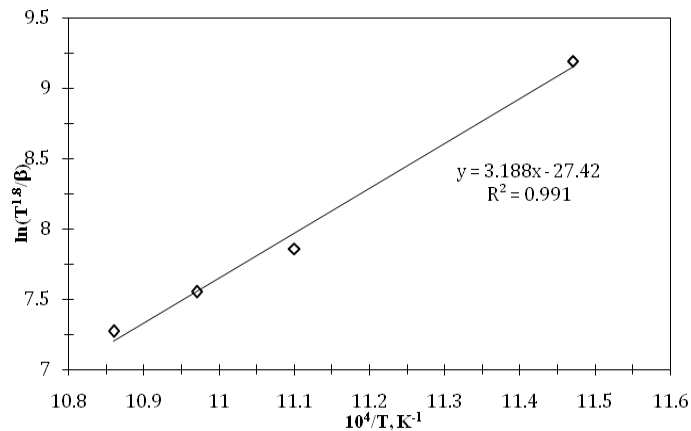

Figure 2. Arrhenius plot for the exothermic peaks of the DSC curves for Al_2O_3 - PTFE.

High-Speed Temperature Scanner (HSTS-1)

Al_2O_3-PTFE system: In the thermogram (Figure 3, left) received for Al_2O_3-PTFE system at a heating rate of 780 °C/min, there is an endotherm in temperature ~360 °C which is corresponding to the melting of PTFE. According to the HSTS data, the PTFE decomposition takes place at about 640 °C close to the Al melting point (Figure 3, right). In the system Al_2O_3-PTFE the decomposition of PTFE and the reaction between Al_2O_3 and PTFE occur almost in the

same temperature range, which is around 800 °C (Figure 4). As can be seen from Figure 3, (left), the interaction between Al_2O_3 and PTFE is exothermic enough and the temperature rise on the thermogram was about 80 °C at heating rate of 780 °C/min. Table 1 summarizes the characteristic temperatures and heating rates for the samples of Al-PTFE, Al_2O_3-PTFE, and PTFE.
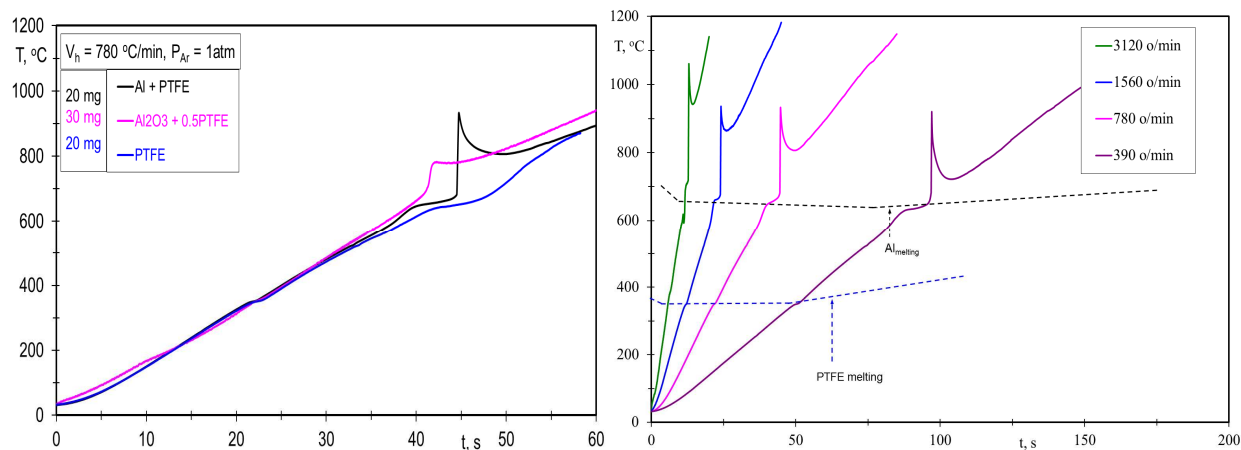

Figure 3. The HSTS curves for (left) Al - PTFE, Al_2O_3 - 0.5PTFE and PTFE at heating rate of 780 °C/min; and (right) Al + PTFE at different heating rates.

Table 1. The characteristic temperatures and heating rates for the samples: Al-PTFE, Al_2O_3-PTFE and PTFE.

Sample	Al - PTFE	Al_2O_3 - PTFE	PTFE	PTFE (DTA)
Mass of sample, (mg)	20	30	20	50
V_h, (°C/min)	780	780	780	20
$T_{PTFE\ melting)}$, (^{o}C)	345-355	350-360	345-355	310-340
$T_{PTFE\ decomposition}$, (^{o}C)	-	-	640-670	460-640
Temperature of starting the reaction: Al_2O_3 - PTFE, (^{o}C)	600	660	-	-
Temperature range of reaction: (Al-PTFE), (^{o}C)	670-810	-	-	-
T_{max}, (^{o}C)	930	780	-	-
ΔT_{max}	240	80	-	-

Al - PTFE system: The interaction between Al and PTFE at the heating rates of 130 – 3200 ^{o}C/min were conducted by using reaction:

$$4Al+3(C_2F_4)_n= 4AlF_3+6C \qquad (3)$$
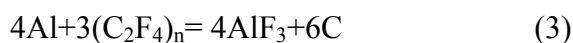
As can be seen from the results presented in Figure 3, (left) firstly PTFE melts at ~ 340 °C. Then the reaction between Al oxide layer with PTFE and its decomposition products occurs at ~ 540-610 °C (depending on heating rate). At the temperatures of about 630-680 °C appears endothermic peak related with the melting of Al. The characteristic temperature dependences on

the heating rate for the system Al – PTFE are shown in Table 2. After melting of Al in all thermograms, we observed sharp exothermic interaction, which is the result of the reaction between melted Al and decomposition products of PTFE. Note, that the reaction temperature is strongly dependent on heating rate.

The next series of experiments were conducted changing the concentration of PTFE in the initial mixture (Al - xPTFE). In this case we observed the analogous qualitative properties (Figure 4), the melting of Teflon at ~340 °C, the pyrolysis of PTFE and interaction between Al_2O_3 and the decomposition products of PTFE, then the melting of Al at 660 °C followed by the intensive exothermic reaction between Al and the decomposition products of PTFE. When decreasing the values of x from 0.125 to 0.0312 the corresponding values of T_{max} and ΔT_{max} are decreasing accordingly from 900 °C to 750 °C and from 240 to 80 °C (Table 3).
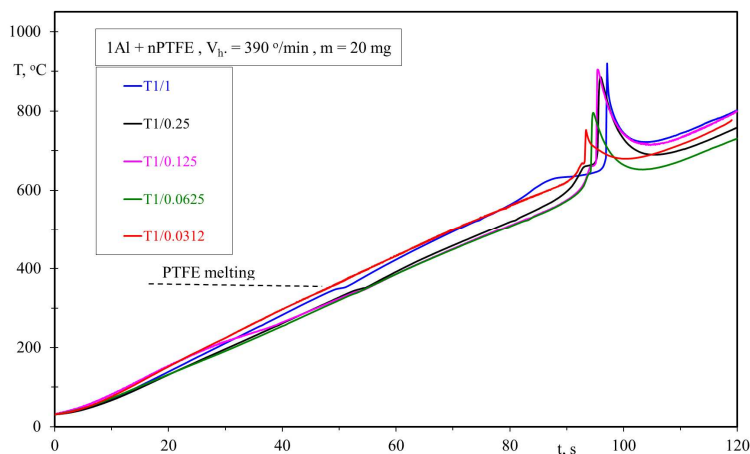

Figure 4. HSTS curves in the system (Al - PTFE) thermograms vs. Al/PTFE ratio.

Table 2. The characteristic temperatures and the heating rate for Al –PTFE system, (m=20 mg).

V_h°C/min	3200	1560	780	390	260	130
Temperature of starting the reaction: (°C)	600	600	600	600	540	610
Ignition temperature of Al - PTFE, (°C)	720-940	670-870	680-810	650-720	700-740	730-770
T_{max}, (°C)	1060	930	930	920	1040	820
ΔT_{max}	230	230	240	250	320	70

Table 3. The characteristic temperatures for the initial ratio of Al/PTFE, (m=20 mg).

Al/PTFE ratio	1/1	1/0.25	1/0.125	1/0.0625	1/0.0312
V_h, °C/min	390	390	390	390	390
Ignition temperature (°C)	600	610	620	620	630
Temperature range of reaction: Al - PTFE (°C)	640-720	670-690	660-720	645-650	670-680
T_{max}, (°C)	920	890	900	790	750
ΔT_{max}, (°C)	260	210	240	140	80

CONCLUSIONS

The highly exothermic reaction between Al_2O_3 and PTFE with activation energy of 265 kJ/mol was identified. The thermodynamic calculations of reaction $Al_2O_3 + 1.5/n(C_2F_4)_n = 2AlF_3 + 3CO$ gives an adiabatic temperature of $T_{ad}=1420K$. This temperature is not sufficient to generate self-sustaining reaction in Al_2O_3 - PTFE system, however can increase the reaction rate during interaction of Al and PTFE, since Al particles always contains thin layer of aluminum oxide. The exothermic Al_2O_3 - PTFE reaction can be observed only at 150 °C/min heating rate or higher. The decomposition rate of PTFE strongly affects to the reaction pathway.

The study shows that the PTFE can potentially remove the oxide layer from aluminum and increase the direct contact area between oxygen and aluminum, which increases the reaction velocity and improves the energy discharge. The HSTS is a powerful tool to investigate the solid-state reactions at high heating rates and opens new opportunities to study the reaction mechanisms under extreme conditions.

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