

Thermal analysis of the mixtures of paraffin with aluminum in wide temperature range

S A Gubin, I V Maklashova and I S Levitskaya

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)
Kashirskoye shosse 31, Moscow 115409, Russia

E-mail: ivmaklashova@mephi.ru

Abstract. The mixtures and composites of wax, paraffin and metals are widely used as energy efficient formulations and phase change materials for heat storage. Aluminum is frequently employed in the formulations of many composite explosives or propellants. Metal fuel additives are used in advanced explosive formulations to achieve higher combustion temperatures and longer pressure pulses. In this project, Al-paraffin wax composite materials were prepared and characterized. The thermal stability of the prepared powders was determined by differential scanning calorimeter, simultaneous thermogravimetry analysis-differential thermal analysis in the temperature range 30-1300°C at atmospheric pressure. The results of differential scanning calorimeter showed that the thermal performance and structure of the composite materials are stable up to 200°C. The paraffin decomposition with an energy release is possible at temperatures over 200°C and the oxidation of aluminum may be at a temperature above its melting point. It is shown that the maximum total amount of heat generated by the thermal decomposition of the composition was at the mass fraction of aluminum of 16% - 18%.

1. Background and the purpose of work

The paraffin as phlegmatizer and the powder of aluminum for improving the energy are widely used in explosives mixtures and rocket propellants [1, 2].

The purpose of work was study the process of thermal decomposition of the mixture of paraffin and aluminum powder micron dispersion by a simultaneous thermal analysis; the estimation of the activation energy of decomposition of paraffin and the determining the optimal percentage of mixture components for using as energy efficient formulations.

Such mixtures are a promising material (phase change materials) in the field of energy saving for thermal batteries. To increase the heat capacity and thermal conductivity of the wax is added powder of aluminum [3, 4]. Thus, the heat of fusion of paraffin wax is used for accumulation of thermal energy in thermal batteries [4], and high values of heat of formation and phlegmatizing properties of wax to allow its use in high-energy formulations [5, 6].

Note that the mixtures of aluminum powder with paraffin are flammable. With the destruction or loss of integrity device possible ignition and combustion of the mixture. Therefore, the study of thermal decomposition of the compositions of paraffin wax and aluminum powder should be performed in a wide range of temperature changes. At low temperatures up to 200°C the information is needed to manage the storage of thermal energy at higher temperatures will be useful for applying



such compositions in energy-intensive compositions for the understanding of their thermal decomposition and ignition of aluminum particles.

If thermal decomposition of paraffin has been studied rather thoroughly [7, 8], the patterns of thermal decomposition of mixtures of paraffin and aluminum powders is studied poorly. Introduction to different quantities of fine and ultrafine aluminum particles in the paraffin changes the density, thermal conductivity, specific heat and other thermophysical and thermodynamic characteristics of the composition. This causes a change in the regularities of thermal decomposition of mixtures of paraffin and aluminum particles.

2. The technique

The thermal stability of the composite materials was determined by differential scanning calorimeter, simultaneous thermogravimetry analysis-differential thermal analysis. The method of simultaneous thermal analysis, which brings together in one dimension thermogravimetric analysis (TGA / DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) gave information about the composition, thermal and oxidative stability of materials, phase transitions, and the kinetics of chemical reactions. The thermal decomposition and the possible interaction of decomposition products of wax and ultrafine aluminum upon heating these compounds was investigated in a wide range of temperature changes (from normal conditions to a temperature of 1300°C).

The heating rates varied from 2°C/min to 50°C/min to estimate the kinetics of processes. The experiments were carried out in air or argon atmosphere in a crucible with the opened or closed cover to estimate the oxidation in various oxidizing environments

3. Results

The analysis of the processes of melting and oxidation of the paraffin and the aluminum is carried out by different heating rate (2 K/min, 10 K/min 20K/min, 50K/min) in temperature range from 30°C to 1300°C in different atmospheres (air and Ar).

Figure 1 shows a typical thermogram of decomposition of a mixture of paraffin and aluminum. In the thermogram can be allocate four temperature ranges, where the Thermal decomposition, namely, there are peaks of heat flow: $T_1 = 40 \div 70^\circ\text{C}$, $T_2 = 200 \div 450^\circ\text{C}$, $T_3 = 600 \div 700^\circ\text{C}$, $T_4 = 1000 \div 1100^\circ\text{C}$.

The first peak of the DSC curves associated with the melting of wax $T_{\text{melt}} = 57^\circ\text{C}$. With increasing heating rate the peak a few shifts to higher temperatures.

Thermal decomposition of the wax begins after 200°C . In the temperature range $T = 200 \div 450^\circ\text{C}$ is an intensive mass loss of wax. The first range in said exothermic peak in the DSC curve is associated with a break C-C bonds in long hydrocarbon molecules and dehydrogenation. At the end of this temperature range is possible oxidation products of thermal decomposition of the wax in air [8]. At higher temperatures, there is an intensive $T \geq 800\text{K}$ oxidation decomposition products wax in air.

Obtained by the method of Kissinger activation energy of decomposition of paraffin $E = 28.2$ kcal/mol in agreement with the experimental data [7- 9].

The kinetics of oxidation and combustion of the aluminum particulate were studied in [10 - 12]. Thermal decomposition aliminum particles decrease with increasing heating rate percentage burn-alumina, wherein while blowing air, this percentage is higher than argon purge. In the presence of air of aluminum powder melting begins at lower temperatures with increasing heating rate.

The figure 2 shows that the curve 4 (16.7% of the mass content of aluminum) is located above the rest in the investigated temperature range. Draws attention to the close location of the curves 4 (16.7%) and 6 (36%). But at high temperatures line 6 is located below the line 4. Therefore, the total amount of heat by thermal decomposition of a mixture of paraffin with a mass content of aluminium 16.7 % (line 4) is higher compared with the composition containing 36% aluminum (line 6).

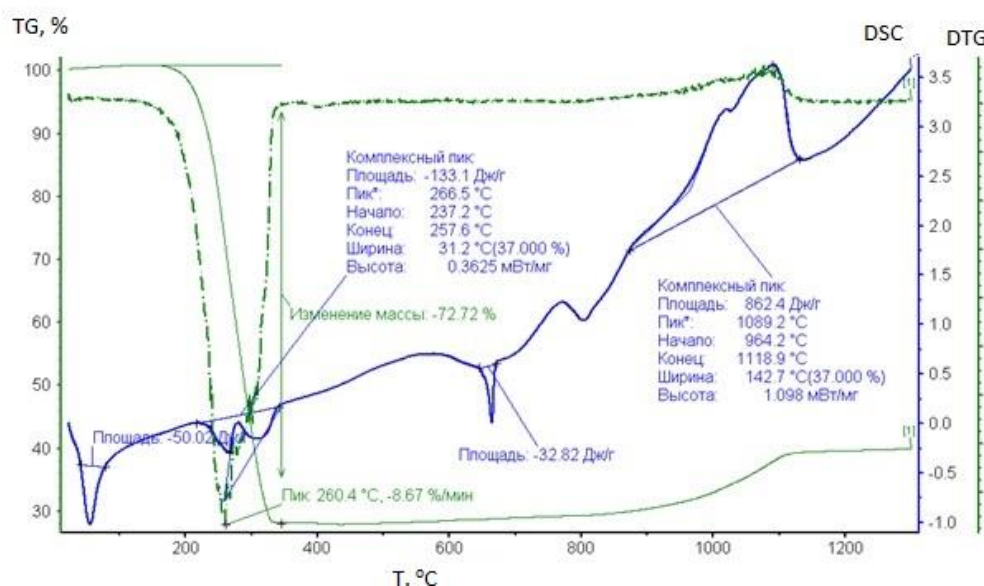


Figure 1. The typical thermogram of Al-paraffin mixture (18% Al) in air, heating rate 10K/min

The conclusion about the maximal condition of energy release of the mixture of paraffin with 16.7% of aluminum is confirmed by Figure 3, which shows the total amount of heat released during thermal decomposition of a mixture of paraffin depending on the mass number of aluminum in the composition.

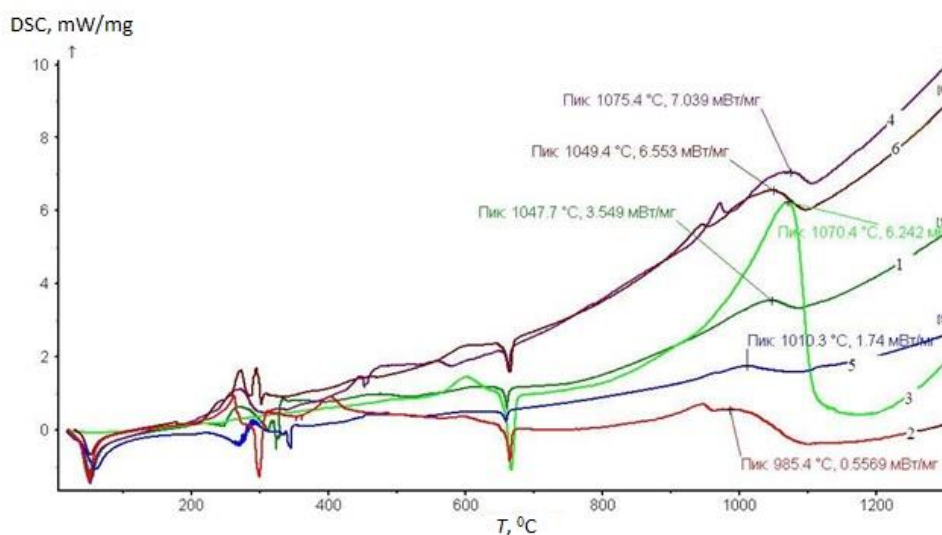


Figure 2. The thermograms of Al-paraffin mixture: 1– 10.2 % Al (closed crucible), 2– 10.9% Al (open crucible), 3– 100% Al, 4– 16.7% Al (closed crucible), 5– 5.2% Al (closed crucible), 6– 36% Al (closed crucible), heating rate 10K/min in air.

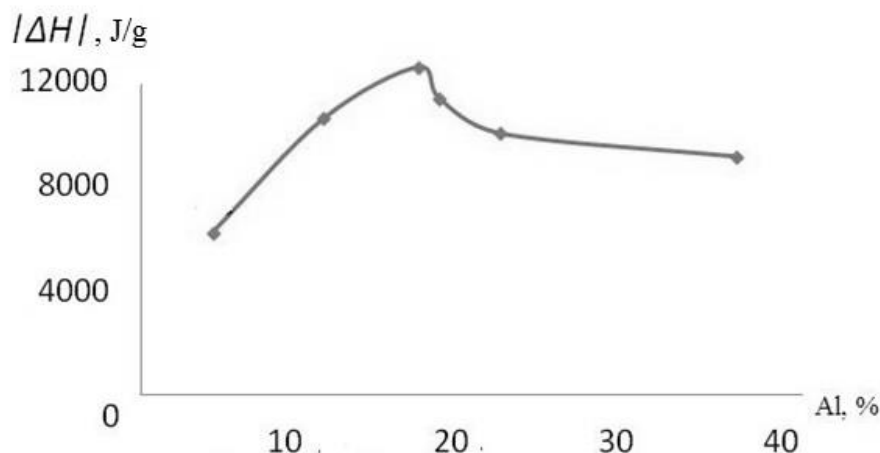


Figure 3. The total amount of generated heat depending on the weight amount of aluminum in the composition.

Mass percentage of aluminum 16.7% is optimal for use in energy-intensive compounds, as a consequence, improving their thermodynamic characteristics (thermal conductivity, heat capacity), due to a uniform warming of the mixture. If the mass of aluminum in the crucible is too large, the metal does not have time to warm up to the temperature of paraffin. When uneven heating of the aluminum particles in the surface layers of the sample are oxidized with the formation of refractory oxide on their surface. This reduces the area of contact of aluminum particles, degradation products of paraffin wax and air. The temperature of the wax becomes higher than the temperature of aluminum particles and there is no reaction of decomposition products of paraffin wax and aluminum particles. Therefore, mixtures with a mass content of aluminum 16%-18% have the highest dissipation by thermal decomposition in comparison with other compounds.

It can be noted that in the crucible without lid energy release is practically not observed. Paraffin vapors freely out of the crucible into the surrounding space. Thus, we can conclude that using the lid of the crucible helps to keep a pair of paraffin in a crucible, and contributes energy to the interaction of the vapour of paraffin with aluminum.

4. Conclusions

1. It is shown that with increasing heating rate melting of wax begins at somewhat higher temperatures.
2. According to the method of Kissinger activation energy of decomposition of paraffin $E=28.2$ kcal/mol.
3. It is shown that the total amount of heat generated by thermal decomposition of wax-aluminum mixtures has the maximum at aluminum content of 16 - 18% mass% due to the best energy performance degradation over a wide range of temperatures.
4. In closed spaces at high temperatures may be a considerable energy release during the decomposition of paraffin with aluminum. This aspect should be considered in designing thermal storage.

Acknowledgments

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