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The study of the effect of aluminum powders dispersion on the oxidation and kinetic characteristics

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Abstract. Differential-scanning calorimetry (DSC) and thermogravimetric analysis (TG) were used to study micro-sized aluminum powder ASD-4 and nano-sized powder Alex. The dependence of the oxidation process on the dispersion of the sample particles is shown. The influence of thermogravimetric conditions on the thermal regime of the process was considered, and its kinetic parameters were determined. Calculations of the activation energy and the pre-exponential factor were carried out.

1. Introduction

Over the past decades, the use of powdered metals is constantly expanding, with the help of which it is possible to improve the energy and performance characteristics of propulsion systems. Aluminum powders have been found wide application as a fuel component in energy condensed systems for various purposes, as well as in space technology [1–3].

The study of the regularities of metal oxidation processes makes it possible to determine the influence degree of both dimensional and structural factors on the reactivity of perspective materials and determine their stability under environmental conditions.

Thermogravimetric study of the influence of phase formation on the kinetics and mechanism of oxidation of aluminum powder doped with calcium was carried out in [4]. The completeness of the conversion of a calcium-doped powder is two or more times higher than that of pure aluminum. The authors [5] investigated the effect of barium on the kinetics of the oxidation of an aluminum-based alloy powder. The comparison of thermograms indicates that the pure aluminum powder up to the melting point oxidizes more vigorously than the alloy. After melting, the alloy powder oxidizes more actively. The maximum exothermal peak of alloy oxidation at 1383 K corresponds to a specific heat release 9026 J/g. Alloying of aluminum with barium increases the completeness and rate of aluminum oxidation. In these studies, the authors did not investigate the effect of aluminum dispersion on the oxidation regularities.

At present nano-sized aluminum powder is widely studied by thermal analyses. But it is also important to know the kinetic characteristics of oxidation of aluminum powder: the activation energy and the pre-exponential factor [6].

Analysis of scientific publications shows that the results of different authors of the kinetic characteristics of metallic powders oxidation differ considerably. It can be assumed that this

discrepancy is due to different methods of aluminum powder production, storage conditions, and the content of impurities.

Despite a wide range of studies of metal powders, the relevance of analyzing the effect of the powder particle size on the behavior of physicochemical processes remains.

The present work is devoted to the study of the effect of aluminum powder dispersion on the oxidation and kinetic characteristics using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG).

2. Experimental research

2.1. Samples
Recently, aluminum nanopowders produced by the electrical explosion of wires method became commercialized industrial product. The aluminum nanopowders are widely studied as the promising components for high energy materials of different types. The most important problem of the wide application of aluminum nanopowders is the dependence of their properties from the production conditions.

Aluminum powders of two brands were studied in this work: micro-sized aluminum powder ASD-4, and nano-sized powder Alex obtained by the electric explosion method with average mass diameters of 7.34 μm and 0.18 μm respectively. The specific surface area was 0.5 m^2/g for ASD-4, and 13.9 m^2/g for Alex. The content of active aluminum in the powders of these grades was 98.0 and 85.8% weight, respectively [7].

2.2. Thermal analysis
Today thermal analysis is one of the most common and widely used laboratory techniques. Combustion researchers exploit thermal analysis to characterize both the stability and ignition of many high energy materials.

However, there are important limitations. The rates of thermal analysis measurements are necessarily much lower than the heating rates occurring in most practical situations involving ignition of reactive materials.

To study the effect of dispersion of aluminum powder on oxidation process, the methods of TG and DSC were used. The experiment was carried out in the temperature range from the standard room temperature up to 1000 °C under heating rates of 5, 10 and 20 C/min in the air flow.

When the temperature changes, the processes in the sample, such as melting, restructuring of the crystal structure, evaporation, oxidation, can proceed with a change in the enthalpy.

In the thermal analysis method, the following notation is adopted – endo-effects (heat absorption) assume to be negative, and exo-effects (heat release) to be positive.

The experiment was performed with NETZCH STA 409 PC/PG equipment.

3. Results and discussion
Based on the TG analysis, it was found that when the samples are heated up to ~500°C, the mass increase due to oxidation practically does not occur. Moreover, when the temperature changes from 200 to 500 °C both for Alex and ASD-4, a decrease in mass (up to 1.7%) is observed. The loss of mass may be related to evaporation of the adsorbed water on nanoparticle surfaces or adsorbed gases desorption.

Experimental studies showed that the intensive oxidation of ASD-4 and Alex in air begins below the melting points of aluminum powders and the rate of heating affects the onset of oxidation. Analysis of the curves in figures 1 and 2 showed that for aluminum powder ASD-4 the onset oxidation temperature, depending on the heating rate, varies from 571 to 576 °C and for Alex varies from 550 to 580 °C.

The process of nonisothermic oxidation for aluminum powder may be divided into two stages: low-temperature, due to heterogeneous reactions between the gaseous oxidizer and solid particle core

[3], with a sharp mass gain, (for ASD-4 – 571–650 ºC, for Alex –550–625 ºC) and high-temperature less intensive stage of oxidation (ASD-4 – 750–830 ºC, Alex – 705–740 ºC), depending on the heating rate. This two-stage character may be related to any of the following phenomena: the periodic cracking of the oxide shell covering the particle metal core [8]; the separate oxidation of different particle fractions (the finest particles are oxidized before metal core melting, while the larger ones react after melting in the same temperature range as the conventional micron-sized powders [9].
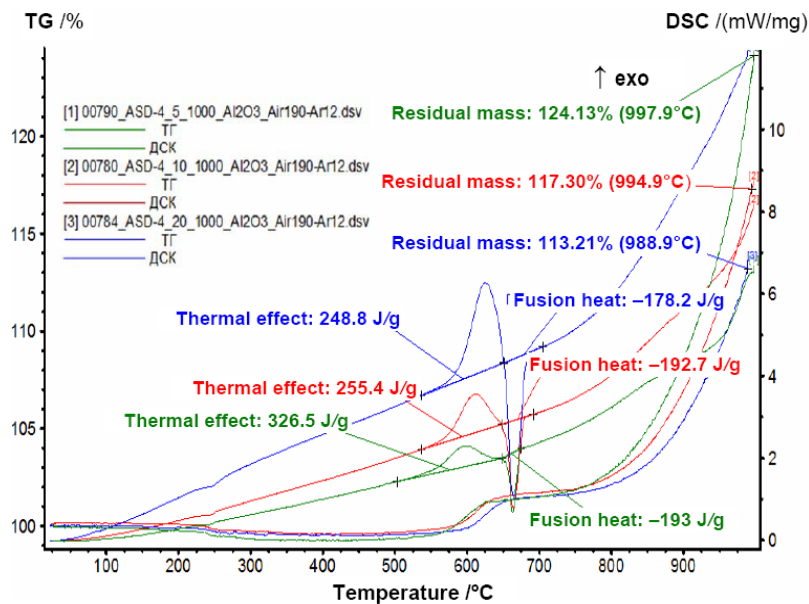

Figure 1. TG and DSC diagrams for ASD-4 at heating rates of 5, 10 and 20 ºC/min.
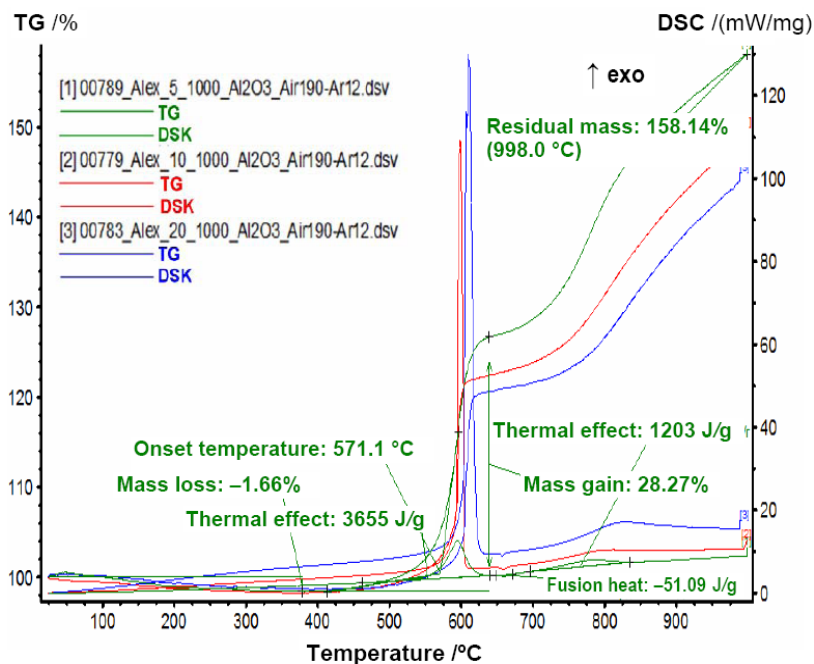

Figure 2. TG and DSC diagrams for Alex at heating rates of 5, 10 and 20 ºC/min.

Changing of the heating rate in the range from 5 to 20 C/min declines the mass gain of aluminum powders: for ASD-4 – from 124.13 to 113.21%; for Alex – from 158.14 to 144.03%. This indicates that at a low rate of heating the oxidation reaction of aluminum powder has time to pass more completely.

Analysis of the results obtained with DSC analysis showed that the energy of heat release during oxidation of ASD-4 aluminum powder decreases from 326.5 J/g to 248.8 J/g with increasing heating rate, becoming more convex but narrow in the shape. Under the above conditions, the melting heat value for ASD-4 varies from –193 J/g to –178.2 J/g. For the Alex brand powder, the energy of heat generation during oxidation changes from 3655 J/g to 3467 J/g as the heating rate increases. The heat of fusion (under identical conditions) for Alex varies from –51.09 J/g to –14.45 J/g.

The generalized results for TG and DSC analyzes are given in tables 1 and 2.

Table 1. Thermophysical characteristics of the ASD-4 oxidation process.

Heating rate ºC/min	First stage of oxidation		Second stage of oxidation		Thermal effect	
	$T_{o.ox}$, ºC	$T_{e.ox}$, ºC	$T_{o.ox}$, ºC	$T_{e.ox}$, ºC	ΔH_{ox}, J/g	ΔH_m, J/g
5	571	635	750	up to 1000	326.5	−193.0
10	576	640	760	up to 1000	255.4	−192.7
20	576	650	830	up to 1000	248.8	−178.2

Note: $T_{o.ox}$, ºC – onset oxidation temperature, $T_{e.ox}$, ºC – end-point oxidation temperature, ΔH_{ox} – thermal effect of oxidation, ΔH_m – thermal effect of melting (fusion heat).

Table 2. Thermophysical characteristics of the Alex oxidation process.

Heating rate ºC/min	First stage of oxidation		Second stage of oxidation		Thermal effect	
	$T_{o.ox}$, ºC	$T_{e.ox}$, ºC	$T_{o.ox}$, ºC	$T_{e.ox}$, ºC	ΔH_{ox}, J/g	ΔH_m, J/g
5	550	625	705	up to 1000	3655.0	−51.1
10	560	610	720	up to 1000	3391.0	−44.1
20	580	625	740	up to 1000	3467.0	−14.5

Translating any processes detected in thermal analysis to practical problems requires a well-justified kinetic model. It is of great practical importance to determine the parameters of the formal kinetics – the activation energy and the pre-exponential factor. These parameters are important for understanding the combustion mechanism and constructing theoretical models of combustion of high-energy materials.

The reaction rate dependence on temperature is established by the Arrhenius equation:

$$K = A \cdot \exp\left(-\frac{E_a}{RT}\right),$$

where K is the rate constant, A is a pre-exponential factor, associated with the probability of collision and E_a is the activation energy.

Based on the results of TG and DSC analyzes, the activation energy (E_a) and the pre-exponent (A) were calculated for the oxidation of aluminum powders by three formal kinetic methods according to the program Kinetics 3 of the NETZCH software (tables 3, 4).

The activation energy and the pre-exponent were obtained using model-free Friedman analysis, Ozawa-Flynn-Wall analysis and ASTM E698 analysis. To determine the activation energy according to the ASTM E698 standard, the peak of the heat flow rate were used without taking into consideration

the type of reaction. Thus an average value of the activation energy was obtained. In the Friedman differential method and the Ozawa-Flynn-Wall integral method, points with the same degree of conversion of all curves (isoconversion) were used to determine E_a without taking into account type of reaction. The data of TG and DSC analyzes for the low-temperature oxidation stage at three heating rates were used to calculate the formal-kinetic parameters.

Preliminary estimates of the formal-kinetic parameters (E_a, A) for aluminum powders of different dispersion at a conversion degree of 0.2 were obtained.

The results of calculations showed the sensitivity of the program to the temperature range selection.

The obtained values of the activation energy and the pre- exponential factor are consistent with the results of [10].

Table 3. Values of activation energy and pre-exponential factor for ACD-4.

Method	Activation energy, E_a, kJ/mol	Pre-exponential factor, $\log(A/s^{-1})$
Friedman analysis	308.55 ± 38.76	18.85
Ozawa-Flynn-Wall analysis	385.65 ± 3.43	23.36
ASTM E698	566.63 ± 6.50	34.25

Table 4. Values of activation energy and pre-exponential factor for Alex.

Method	Activation energy, E_a, kJ/mol	Pre-exponential factor, $\log(A/s^{-1})$
Friedman analysis	449.21 ± 48.23	27.51
Ozawa-Flynn-Wall analysis	358.64 ± 26.86	21.88
ASTM E698	581.96 ± 150.70	35.77

4. Conclusions

In the course of this work, thermogravimetric studies showed that aluminum nanopowder Alex provides more full reaction of oxidation than ACD-4. When heated, the mass gain of aluminum oxide for Alex in the first stage of oxidation is 1.3 times higher than that of ASD-4 under the identical conditions and the same heating rates. In the second stage, the oxidation rate the samples of ASD-4 and Alex are close. At the same time, ASD-4 has a lower degree of sample transformation even when 1000 °C. The TG and DSC analyzes presented the following results: a) the effect of the aluminum powder dispersion on the oxidation process – for Alex all the oxidation processes shift to the lower temperature region; b) the effect of the heating rate on the oxidation onset and the energy of heat release. The use of modern kinetic evaluation methods for complex reactions allows to select formal-kinetic model and to determine activation parameters. The activation energy and the pre-exponential factor were calculated. Obtained results are of interest in describing the combustion processes of aluminum powders or any condensed materials containing aluminum.

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