Studying the fire hazard properties of multi-walled carbon nanotubes by the method of synchronous thermal analysis

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Abstract. The present paper considers oxidation of multi-walled carbon nanotubes at different heating rates and temperatures to ensure the process in the kinetic region. The nanotubes were analyzed by the method of synchronous thermal analysis. Experiments were carried out at different heating rates: 5, 10 and 20 °C/min. As a result, the character of thermogravimetric and differential thermogravimetric curves was determined, and thermograms were constructed, thereby allowing to define weight loss stages and establish exact weight loss values at a programmed temperature increase. Besides, the temperature characterized by the maximum weight loss rate was established. Differential scanning calorimetry revealed the maximum temperature of endothermic and exothermic peaks, as well as changes in thermal effects (enthalpy changes). The most important indicators of fire hazard of the multi-walled carbon nanotubes – ignition and self-ignition temperature – were determined. The ignition temperature was approximately equal to the temperature of the beginning of the thermal distortion of the sample in the air – 553.7, 578.6 and 584.3 °C for the heating rates of 5, 10 and 20 °C/min, respectively. The self-ignition temperature corresponded to the temperature of the maximum yield of volatiles – 627.5, 651.9 and 670.8 °C for the heating rates of 5, 10 and 20 °C/min, respectively.

1. Introduction
Due to economic reasons, multi-walled carbon nanotubes (MWCNTs) are the most relevant from the point of view of carbon materials applications. Currently, the total global production of carbon materials is about 1 million tons per year [1]. The increase in the productive capacity inevitably entails an increase in the area of accommodation of the finished product. In this regard, the problem of combustion and explosion of the carbon materials is of particular relevance.

When considering the explosion and fire hazard of dust, special attention is usually paid to its explosive properties [2-16], which are known since the 18th century [2-4]. Explosion and fire hazard of dust (dust cloud) and a dust cloud characterize the following indicators: maximum explosion (over)pressure, maximum rate of overpressure rise, index of fire and explosion hazard (the Kst parameter, or deflagration index), minimum explosive concentration (low explosion limit), normal flame propagation speed, self-ignition and ignition (fire) temperatures, smoldering and layer ignition, heat of combustion, minimum ignition energy, limiting oxygen concentration, burning time, safe
experimental maximum clearance, flame emissivity, minimum phlegmatizing concentration of gaseous deterrents, toxicity of combustion products, ability to burn when in contact with water, oxygen and other substances and to spontaneous combustion and exothermic decomposition, and combustibility group [2-18].

The requirements for determining the indicators of explosion hazard of substances and materials are set out in the paper [19]. Kinetics of thermal oxidation of the carbon nanomaterials was studied by differential thermal analysis in air [20]. However, the fire hazard indicators are not considered in these works.

Considering the aforementioned, the aim of the present work was to study the oxidation of MWCNTs in the air atmosphere, and determine ignition and self-ignition temperatures by a thermal analysis method.

2. Experimental part

“HW NANO” MWCNTs (Xuzhou, Jiangsu, China), with a purity of 98%, average diameter of 0.83 nm and length of 1-2 um were employed in experiments. A corundum crucible with a volume of 85 µL was used, in which 3 to 4 mg of the MWCNTs was loaded.

The method of synchronous thermal analysis makes it possible to measure the dependence of weight changes in the test material and the inert sample (for comparison) and heat flow on temperature (time). It is successfully used to study the heat resistance of flame retardants, as well as the indicators of fire hazard of substances and materials. In the present research, this analysis was implemented in an air medium at the heating rates of 5 (experiment 1), 10 (experiment 2) and 20 °C/min (experiment 3). The measurement chamber was purged with a mixture of oxygen and nitrogen to create an environment as close to air as possible (20% / 80%). The MWCNTs were placed in an alumina crucible without lid.

A series of experiments were carried out using an STA 449 F5 Jupiter synchronous thermal analyzer (NETZSCH, Selb, Germany). This instrument is included into the State Register of Measuring Instruments and has a certificate of approval, as well as a valid certificate of verification. It represents a measuring complex that combines the functions of high-precision analytical scales and a differential scanning calorimeter.

The thermogravimetry (TG) analysis allows to determine the stages of weight losses based on TG curves constructed, and to establish the exact weight loss values at a programmed temperature increase. From differential TG (DTG) curves, it is possible to establish temperature characterized by a maximum weight loss rate. The data presented by differential scanning calorimetry (DSC) curves allow to reveal the maximum temperatures of endothermic and exothermic peaks, as well as changes of thermal effects (enthalpy changes).

The test results were obtained on certain graphics, the processing of which was performed using the Proteus Thermal Analysis software (NETZSCH).

3. Results and discussion

The graphical results (TG and DTG curves) of the synchronous thermal analysis are presented in figures 1-3.

Up to 110 °C, the weight loss areas are associated with the evaporation of adsorbed water. The weight loss in the temperature range of 110-500 °C is negligible. This range represents a section of the thermal stability of the MWCNTs. In the temperature range of 500-650 °C for experiment 1, 500-720 °C for experiment 2 and 500-810 °C for experiment 3, the weight loss caused directly the process of carbon oxidation. The most intense losses can be observed in the temperature ranges of 550-650 °C (experiment 1), 550-730 °C (experiment 2) and 550-810 °C (experiment 3), corresponding to the MWCNTs combustion process.
Exothermic reactions occur in the temperature range of 110-649.9 °C for experiment 1, 110-727.8 °C for experiment 2 and 110-810.8 °C for experiment 3. The graphs of the temperature dependence of heat have irregular shape with many peaks: at 550, 630 and 650 °C for experiment 1, at 550, 650 and 730 °C for experiment 2, and 550, 670 and 810 °C for experiment 3. The process is accompanied by significant weight losses in the samples. The most intense losses take place in the temperature range of 500-650 °C for experiment 1, 500-720 °C for experiment 2, and 500-810 °C for experiment 3. The enthalpy of the MWCNTs was found to be 52,820, 39,373 and 25,920 J/g for experiment 1, 2 and 3, respectively. Thus, the lower the heating rate, the higher the heat of nanotubes combustion.

The parameters of the TG, DTG and DSC curves are given in Table 1.
Figure 3. Graphical results of the synchronous thermal analysis at 20 °C/min.

Table 1. Parameters of the TG, DTG and DSC curves of experiments 1-3.

| No. | Characteristic                  | Experiment 1     | Experiment 2     | Experiment 3     |
|-----|--------------------------------|------------------|------------------|------------------|
| TG 1| Temperature of weight loss     | 553.7 °C         | 578.6 °C         | 584.3 °C         |
|     | beginning                      |                  |                  |                  |
| TG 2| Temperature of weight loss     | 649.9 °C         | 727.8 °C         | 810.1°C          |
|     | ending                         |                  |                  |                  |
| DTG | Weight loss rate               | 8.03 %/min       | 7.71 %/min       | 7.38 %/min       |
|     | Peak weight loss               | 627.2 °C         | 703.1 °C         | 780.0 °C         |
| DSC | Enthalpy                       | 52,820 J/g       | 39,373 J/g       | 25,920 J/g       |
|     | Peak                           | 627.5 °C         | 651.9 °C         | 670.8 °C         |

As can be seen from the table, the heating rate affects the temperature of the beginning and the ending of the weight loss: an increase in the heating rate leads to an increase in the temperature boundaries of this process.

The ignition temperature is the lowest temperature of the substance, at which vapors above the surface of the combustible substance are released at such a rate that leads to the ignition by the influence of an ignition source.

The self-ignition temperature is the lowest temperature of the combustible substance; while heating, there is a sharp increase of rate of exothermic volumetric reactions, leading to the appearance of a fiery combustion or explosion.

These indicators are the most important indicators of fire and explosion hazard. The studies carried out by the method of synchronous thermal analysis, made it possible to determine these indicators for the MWCNTs. The ignition temperature was found to be approximately equal to the temperature of
the beginning of the thermal distortion of the sample in the air. The temperature of self-ignition corresponds to the temperature of the maximum volatile yield. The data obtained on these temperatures are presented in Table 2.

| Heating rate, °C/min | Ignition temperature, °C | Self-ignition temperature, °C |
|----------------------|--------------------------|-----------------------------|
| 5                    | 553.7                    | 627.5                       |
| 10                   | 578.6                    | 651.9                       |
| 20                   | 584.3                    | 670.8                       |

4. Conclusion

The oxidation of the MWCNTs at different heating rates was studied by the synchronous thermal analysis method.

As a result of the experiments, it was found that this method is applicable not only to determine the technological properties of the MWCNTs, but also some indicators of fire and explosion hazard. Thus, the ignition and self-ignition temperatures of the MWCNTs determined at different heating rates were respectively found to be 553.7 and 627.5 °C for experiment 1, 578.6 and 651.9 °C for experiment 2, and 584.3 and 670.8°C for experiment 3. The average self-ignition temperature of the MWCNTs in experiments 1-3 was 572.2 °C, whereas their average self-ignition temperature was 650.1 °C.

The temperature limits of the beginning and ending of the samples weight loss were also different: from 553.7 to 649.9°C for experiment 1, from 578.6 to 727.8°C for experiment 2, and from 584.3 to 810.1°C for experiment 3. Furthermore, the enthalpy of the MWCNTs was found to decrease with increasing the heating rate.

Thus, it can be concluded that an increase in the heating rate leads to an increase in the ignition and self-ignition temperature, an increase in the weight loss temperature range, and a decrease in enthalpy.

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