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ZH. YELEMESSOVA[1,2], K. KAMUNUR[1,2],*
M. K. ATAMANOV[1,2], B. T. LESBAYEV[1,2], R. SHEN[3]

[1]Al-Farabi Kazakh National University, Almaty, Kazakhstan,
[2]Institute of Combustion Problems, Almaty, Kazakhstan,
[3]Nanjing University of Science and Technology, Nanjing, China.
*E-mail: yelemessova.zh@gmail.com

INVESTIGATION OF THE TRANSITIONAL METAL OXIDES EFFECTS ON COMBUSTION AND THERMAL CHARACTERISTICS OF AN/Mg/C-ACTIVATED CARBON COMPOSITES

Abstract. Ammonium nitrate (AN)-based compositesof activated carbonwith metal-oxide have attracted a considerable amount of attention due to the clean burning nature of AN as an oxidizer. However, ammonium nitrate has several major problems, namely, poor ignitability, low burning rate, low energy and high hygroscopicity. The addition of activated carbon and different transitional metal oxides proved to be effective in improving the burning characteristics of AN-based composites. Activated carbon composites were combusted in the atmospheric air and the burning rates were determined. The use of the activated carbon as a fuel allowed the ignition of the AN/Mg/C composites at a lower temperature. Thethermo-gravimetric/differential thermal analysis (TG/DTA) method for investigation of the effect of metal oxides addition tothe AN/Mg/C- carbon based composites for thermal decomposition characteristicswas used.

Keywords: ammonium nitrate, activated carbon composites, burning characteristics, transitional metal oxides, thermal decomposition.

Introduction. Metal-organic frameworks (MOFs) - one of the interesting directions in a wide field of application. The porous crystalline structure attracts attention due to its high specific surface characteristics and the possibility of changing their physicochemical properties by introducing metal centers [1]. However, the process for preparing these bulk polymers is expensive and multistage. In this connection, it is of interest to search for alternative methods for obtaining bulk materials, one of which are structures based on graphene oxide frameworks (GOFs). The growing popularity of multilayer graphenes is due to the uniqueness of their physical and chemical properties. A promising, simple and cost effective method is the production of GOFs from plant wastes like rice husk or walnut shell.

Metal–organic frameworks (MOFs) have attracted great attention because of their intriguing molecular topologies and potential applications in chemical separation,gas storage, drug delivery, catalysis and chemical sensor technology [2]. Particularly, MOFs could also be potential energetic materials because of their high densities and high heats of detonation. For example, Hope-Weeks and co-workers recently reported two hydrazine-perchlorate 1D MOFs [$(Ni(NH_2NH_2)_5(ClO_4)_2)n$ (NHP), and $(Co(NH_2NH_2)_5(ClO_4)_2)n$ (CHP)] with linear polymeric structures[3] which were regarded as possibly the most powerful metal-based energetic materials known to date, with heats of detonation comparable with that of hexanitrohexaazaisowutzitane (CL-20; about 1.5 kcal·g^{-1}). Unfortunately, these coordination polymers were highly sensitive to impact deriving from their low rigidity characteristic of such linear polymeric structures, which makes practical use infeasible.

Understanding the thermal characteristics of AN and mixtures ofANwith combustibles and additives is necessary for enabling its general use in potential new applications, such as propellants and gas generators. Consequently, this study aimed to understand the mechanism of decomposition of AN-based mixtures with an emphasis on the analysis of the gases that evolve from AN, carbon, and metal oxide mixtures [4-7].

EXPERIMENTAL PART

Materials and Samples. Activated carbon (these activated carbons were obtained in the Laboratory of Functional Nanomaterials of the Institute of Combustion Problems, Almaty, Kazakhstan) with metal oxides were mechanically activated in a ball mill (45 min). Ammonium nitrate was used as an oxidizer in the condensed mixture with a diameter of 212-250 µm. Magnesiumwas used as a fuel, and its diameter was 200 µм. The diameter of the metal oxide particles was 60-70 µm, and it acted as a catalyst. Nitrate cellulose was used as a binder.

The method of determining the temperature of burning of structures. The combustion temperature was measured by an optical pyrometer. Optical pyrometer brand PCE 892 is designed to measure temperature from -50 to 2200^{o}C. Two built-in lasers provide accurate sight of the device on the object with an optical ratio of 50:1, which ensures the accuracy of pointing the device at the object and carrying out non-contact measurements of the most compact objects.The temperature measurement error depends on the measured temperature range. When measuring temperature from 20^{o}C to 500^{o}C, the measurement error is ±1 %, from 500 to 1000^{o}C, ±1,5%, and at temperatures above 1000^{o}C±2 %.

High-speed video recording of the combustion process of pyrotechnic compositions. The frames of high-speed filming of the Casio Exilim Ex-f1camera recorded the combustion processes of gas-generating compositions. A unique feature of the camera is the possibility of high-speed photo (up to 60 frames per second at 60 frames per series) and video (up to 1200 frames per second) shooting. The camera allows you to save pictures not only in the format 33 JPEG, but also in DNG format, which is relatively uncommon in cameras of this class.

Measurement of Thermal Decomposition Behavior. Thermal analysis is a quick and effective way to study thermal ignition of energetic materials. Characteristics of thermal decomposition are determined and studied by using thermo gravimetric/differential thermal analysis (TG-DTA) in the temperature range of 40–900°C. The equipment operates in atmospheric pressure in a stream of nitrogen (300 cm^3/min). TG-DTA works with the heating rate of 10 K·min^{-1}.

RESULTS AND DISCUSSION

Combustion characteristics. Figure 1 shows the phenomena of combustion of AN/Mg/C-based activated carbon compositions in the atmospheric air. Activa-

Figure 1 – Burning of pyrotechnic compositions: a) AN/Mg/Nlac, b) AN/Mg/Activated carbon(FeO-2%)/Nlac, c) AN/Mg/Activated carbon (FeO-5%)/Nlac, d) AN/Mg/Activated carbon(NiO-2%)/Nlac, e) AN/Mg/Activated carbon(NiO-5%)/Nlac

ted carbon has been considered as a technological additive capable of working as a promotion agent which has a high activity, high specific surface area and good recovery ability.

It should be noted, that the combustion system is stable and has a laminar flame, accompanied by the release of a large amount of heat with a combustion temperature of approximately 1200°C, and has no solid combustion products.

Analysis of the results showed an increase in the burning rate composite compositions by adding different concentrations of activated carbons with metal oxides (figure 2). Analysis of the linear combustion rate of this sample showed the highest result.

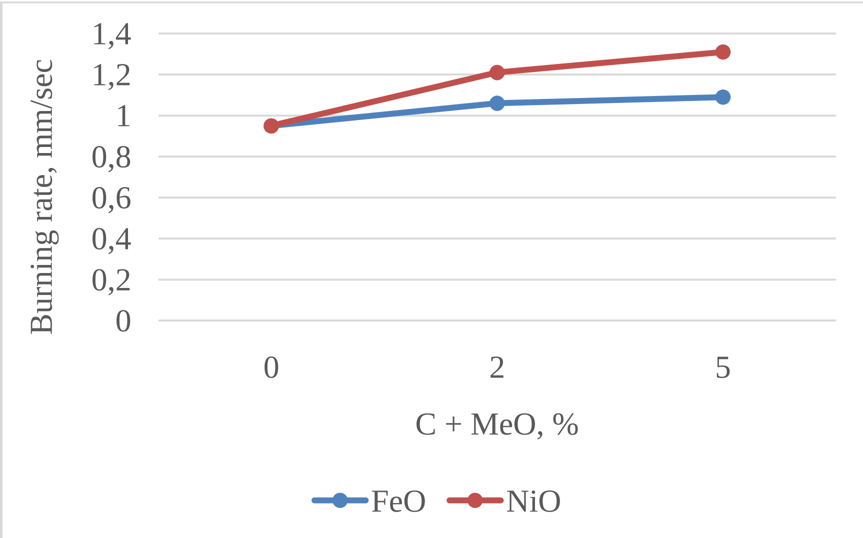


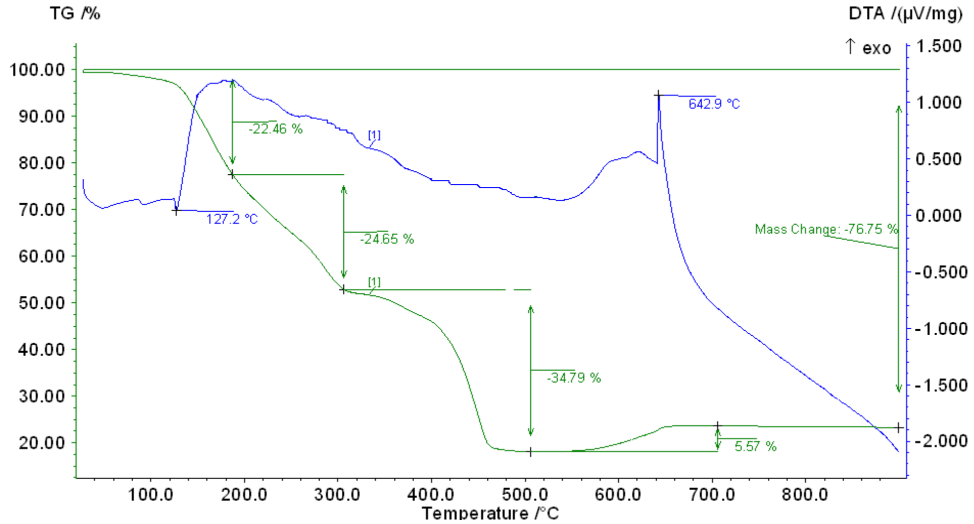
Figure 2 – Dependencies of the burning rates of AN + Mg +Nlac (FeO) and AN + Mg + Nlac (NiO) on the concentration C+MeO,%

The combustion temperature andthe burning rate of activated carbon compositions

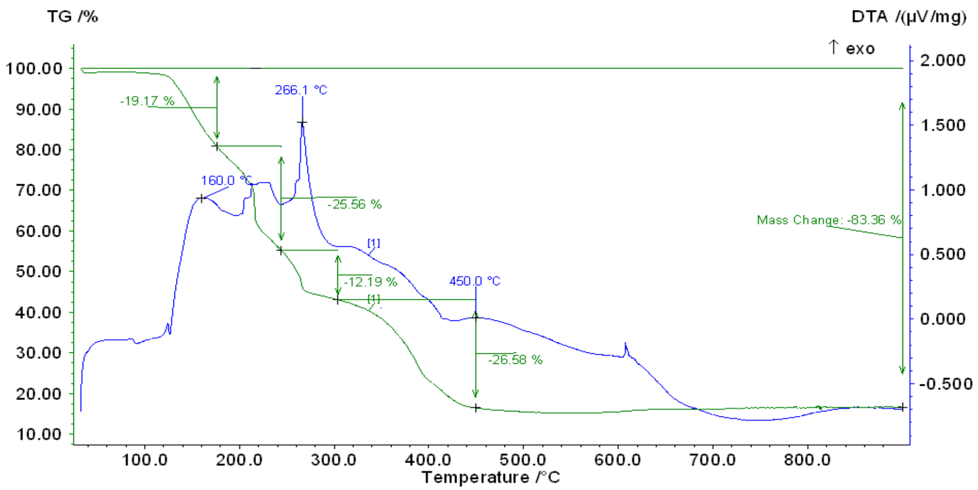
№	Samples	Ratio, %	T, °C (combustion temperature)	U [mm/s] Burning rate
1	AN + Mg + Nitrolac	80/15/5	906	0,950
2	AN + Mg + Act.carbon (FeO-2%) + Nlac	80/10/5/5	944	1,062
3	AN + Mg + Act.carbon (FeO-5%) + Nlac	80/10/5/5	1070	1,097
4	AN + Mg + Act.carbon (NiO-2%) + Nlac	80/10/5/5	1100	1,215
5	AN + Mg + Act.carbon (NiO-5%) + Nlac	80/10/5/5	1240	1,318

Table shows the results of the combustion temperature and combustion rate of composites based on activated carbon.

Characteristics of thermal decomposition. Thermogravimetric analysis (TGA) is a thermal analysis technique, which consists in measuring mass changes of a sample at the same time with increasing temperature in a controlled atmosphere. Results were recorded as weight loss – time (for isothermal analysis) or mass loss-temperature (for analysis made with a constant heating speed). The instrument used for Thermogravimetric analysis was TGA Q5000 IR, TA Universal Analysis, the melting crucible was made of platinum, the gas was 5.0 purity air, the temperature range 40-900°C and the heating rate was 10°C/min (figure 3).



a)



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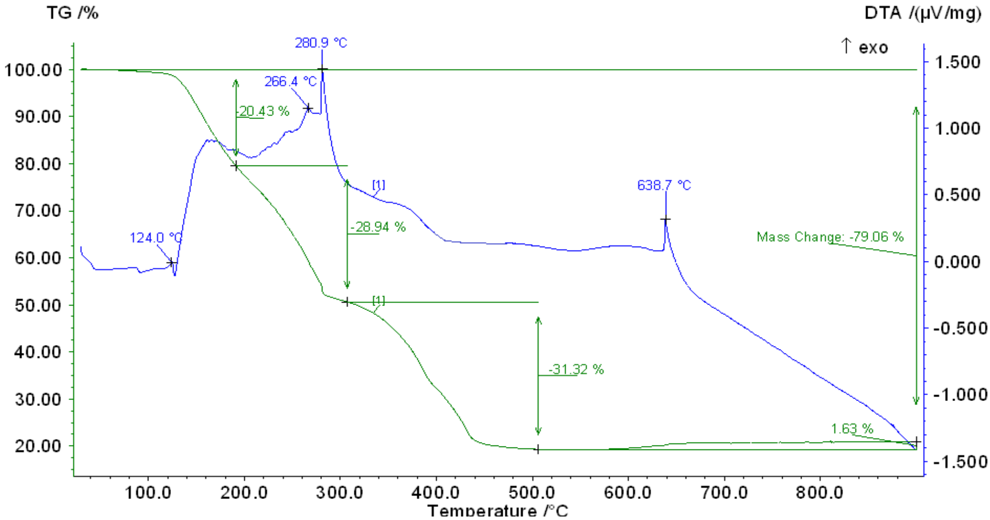
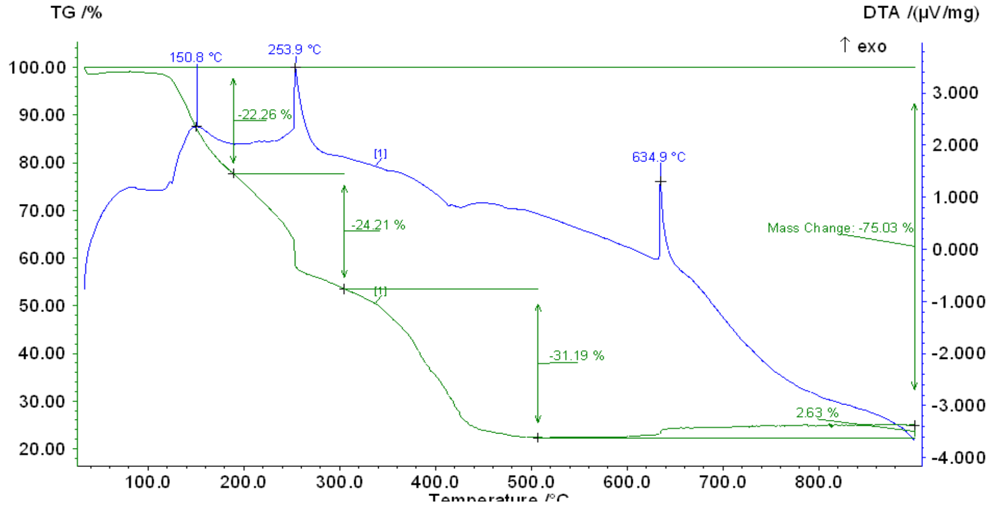


c)



d)

Figure 3 – The results of thermogravimetric and differential thermal analysis of the composite materials: a) AN/Mg/Nlac, b) AN/Mg/Nlac/C, c) AN/Mg/Nlac/AC(FeO), d)AN/Mg/Nl/AC(NiO)

In the figure (3a), we investigated the condensed system AN/Mg/Nlac. Here, the use of ammonium nitrate as an oxidant has affected the melting point of the fuel. The melting point of magnesium decreased from 659 to 642 °C. Thus, it improved the ignition system. In the figure (3b)AN/Mg/Nlac/C, adding activated carbon (C) to this condensed system reduces the phase exchange, melting and decomposition temperatures of ammonium nitrate. The phase exchange of ammonium nitrate ranges from 127 to 122°C, the melting point reduced from 169 to 160°C, and the decomposition temperature increased from 200 to 280°C. At the same time, carbon oxidation (266°C) occurs.The figure (3c) shows AN/Mg/Nl/AC(FeO) system, in this figure, the condensed system is often used for pyrotechnic compounds and detonation. To accelerate the operation of the system and its stabilization, various transition metal oxides were used. The combination of FeO with the condensed system stabilized the composition of the system. This is very effective for pyrotechnic compounds.The figure (3d) shows the AN/Mg/Nl/AC (NiO) condensed system. The adding of NiOto this compound reduces the melting point of ammonium nitrate from 169 to 150°C. This willspeed up the burning system (266 → 253 °C). Consequently, nickel oxide plays an important role as a catalyst in this system.

Conclusion. Application of the activated carbon as a fuel for the pyrotechnic compositions increases the burning rate and condensed system reduces the phase exchange, melting and decomposition temperatures of ammonium nitrate. Addition of metal oxides stabilizes the composition of the system and increases the burning rate significantly. Consequently, nickel oxide can be a catalyst inAN/Mg/C condensed system.

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Резюме

Ж. К. Елемесова, К. Камунур, М. К. Атаманов, Б. Т. Лесбаев, Р. Шен

АКТИВТЕЛГЕН КӨМІРТЕК НЕГІЗІНДЕГІ AN/Mg/C КОМПОЗИТКЕ АУЫСПАЛЫ МЕТАЛЛ ОКСИДТЕРІНІҢ ТЕРМИЯЛЫҚ ЖӘНЕ ЖАНУ СИПАТТАМАЛАРЫНЫҢ ӘСЕРІН ЗЕРТТЕУ

Аммоний нитраты негізіндегі металл оксиді бар белсендірілген көмірдің композиттік құрамы таза жану табиғатына байланысты тотықтырғыш ретінде айтарлықтай көңіл бөледі. Алайда, аммоний нитратында бірнеше негізгі мәселелер бар, баяу тұтанғыш, төмен жану жылдамдығы, төмен энергия және жоғары гигроскопиялылық. Белсендірілген көмір мен әртүрлі ауыспалы металл оксидтерін қосу AN негізінде композициялардың жану сипаттамаларын жақсарту үшін тиімді болды. Белсендірілген көміртекті композиттер атмосфералық ауада жағылды және жану жылдамдығы анықталынды. Белсендірілген көмірді отын ретінде пайдалану AN/Mg/C композиттерінің төмен температурада тұтануына мүмкіндік берді. Термогравиметриялық/дифференциалды термиялық талдау әдісі (TG/DTA) термиялық ыдырау сипаттамалары мен көміртегі негізіндегі AN/Mg/C композиттеріне металл оксидтерінің қосылуының әсерін зерттеу үшін қолданылды.

Түйін сөздер: аммоний нитраты, композитті белсендірілген көмір, жану сипаттамалары, ауыспалы металл оксидтер, термиялық ыдырау.

Резюме

Ж. К. Елемесова, К. Камунур, М. К. Атаманов, Б. Т. Лесбаев, Р. Шен

ИССЛЕДОВАНИЕ ЭФФЕКТОВ ПЕРЕХОДНЫХ МЕТАЛЛИЧЕСКИХ ОКСИДОВ НА ГОРЕНИЕ И ТЕРМИЧЕСКУЮ ХАРАКТЕРИСТИКУ АКТИВИРОВАННЫХ УГЛЕРОДНЫХ НА/Mg/С КОМПОЗИТОВ

Композитный состав активированного угля с металл оксидом на основе нитрата аммония (НА) привлекает значительное внимание из-за природы чистого горения в качестве окислителя. Однако, нитрат аммония - имеет несколько основных проблем: медленная воспламеняемость, низкую скорость горения, низкую энергию и высокую гигроскопичность. Добавление активированного угля и различных переходных металл оксидов оказалось эффективным для улучшения характеристик горения композиций на основе НА. Активированные углеродные композиты сжигались в атмосферном воздухе и были определены скорости горения.Использование активированного угля в качестве топлива позволило воспламенить композиты НА/Mg/С при более низкой температуре. Метод термогравиметрического/дифференциальнотермического анализа (ТГ/ДТА) использовался для исследования влияния добавок оксидов металлов на композиты НА/Mg/С на основе углерода для характеристик термического разложения.

Ключевые слова: нитрат аммония, композитный активированный уголь, характеристики горения, переходные металл-оксиды, термическое разложение.