ABSTRACT

to obtain the degree of Doctor of Philosophy (PhD) prepared dissertation in the specialty 6D073900 – Chemical Technology of Explosives and Pyrotechnics on the theme

Obtaining and investigation of composite materials for flameless heaters

Assessment of the current state of a scientific or scientific and technical problem. In recent years, flameless heaters have been in great demand in cases where it is impossible to use fire, electricity or natural gas, outdoors, in the field, or the use of these heat sources is limited due to natural and various adverse factors. To equip such autonomous heating devices, chemical powders based on energy-intensive metals (magnesium, calcium, iron, aluminum, etc., or mixtures thereof) capable of carrying out exothermic reactions are used. Classical types are widely used in military places for heating or cooking.

Flameless heaters are also widely used in medicine. Due to the effect of intense heating, thermal products based on flameless heaters are an indispensable first aid tool for relieving unpleasant and painful sensations in rheumatism, arthritis, osteochondrosis, bruises and fractures.

The exothermic powders that make up thermal prototypes need to be improved over time depending on the type of application. According to scientific research, the classic flameless type of heater is not without its drawbacks.

The exothermic reaction powder mixture is mainly made by adding water to magnesium and magnesium-based additives. Most powdered impurities are obtained in microns. The micron composites of flameless heater formulations prevent uniform heat distribution during the redox process.

In addition, the main components of these composites can be replaced with calcium carbonate, sodium carbonate, calcium oxide and aluminum powders. This is because the standard enthalpy of combustion of a unit of aluminum is 7.4 Kcal/g, which is much higher than that of Mg. The use of aluminum powders also has a number of advantages, such as high performance, low cost, safety of use, transportation, storage, disposal, minimum weight and long shelf life.

Justification and initial data for the development of the thesis. Today, the use of flameless heaters for heating various liquids or solids in field conditions by activating chemical (exothermic) materials with water or air is becoming widespread. The powder mixture for conducting an exothermic reaction is based mainly on magnesium, iron and additives based on them. In addition, the basic composition of these composites can also be replaced or supplemented with powders of calcium carbonate, sodium carbonate, calcium oxide and aluminum.

Based on literary sources and studying the existing pyrotechnic powders, one can also notice a number of their shortcomings.

The main part of the composition of existing flameless heaters consists of large particles, therefore, it interferes with the uniform distribution of intense heat at the stage of exposure to the redox process. The oxidation of coarse powder is intense only at the initial stage of the reaction, which inhibits the process of heat

exchange with the substance to be heated, thus indicating a significant disadvantage.

Another disadvantage is that a heating device that produces heat as a result of oxidation by an exothermic reaction can be flammable or prone to corrosion. That is, there is a high probability of limiting the expiration date.

Taking into account all the shortcomings of the previously studied flame retardant heaters, in this dissertation work, in order to improve these shortcomings, scientific research is carried out and the creation of new composites that meet modern requirements is envisaged.

Justification of the need to conduct this research work.

The dissertation aims to develop flameless heating sources with high efficiency. The results of the research show that a new powder mixture based on aluminum and calcium oxide has high reactivity and can be used as a flameless heater. The mechanochemical treatment (MChT) of this mixture improves its kinetic and thermodynamic properties, which contributes to increasing the efficiency of the reaction. By studying the influence of different parameters of MChT on the reaction process, we can optimize the conditions for the exothermic reaction and enhance its effectiveness. These findings can be applied to develop new technologies in energy, industrial, and other sectors where high efficiency and flameless heating are essential.The aim of this research is to develop a new powder blend of chemical compounds based on aluminum and calcium oxide, and to investigate its impact on the reactivity and thermal efficiency of a novel exothermic composite through the use of mechanical processing techniques.

Data on patent studies and their conclusions on the planned scientific and technical level of development. During the implementation of the dissertation work, a review of the scientific, technical and patent literature was carried out, as a result of the analysis of the patent literature, it can be seen that the composition of currently existing flameless heaters consists only of magnesium, calcium, iron or their impurities. The size dimensions of these traditional formulations are large microns. It can be noted that no data on highly dispersed composites and the use of activation or composition modification methods were found in the patent literature.

Metrological support of the dissertation. In the course of research work, Metrological support was covered by the use of modern physicochemical methods of analysis performed using 9 certified methods, measuring instruments, equipment and instruments tested by the state standard bodies of the Republic of Kazakhstan.

Relevance of the research topic. It is envisaged to conduct research on the development of new energy-efficient materials, primarily in connection with the importance of their practical application in various fields. Research in the field of creating such materials includes volumetric synthesis, engineering and materials science, as well as microscopic research in the field of molecular dynamics and structure formation. Although Energy Materials began to be used practically from the early period, modern pyrotechnic mixtures, explosives require a lot of research and scientific updates.

In particular, the production of flamethrowers, which are used today in field conditions, without access to a current source or in accidentally unfavorable conditions, also requires research to improve due to modern requirements. In particular, the safety, environmental friendliness of the base metals included in the composite, and the unrestricted or availability of reserves in nature.

To this end, the research area of the dissertation is the replacement of traditionally used magnesium or iron powders in the composition of a flameless heater with aluminum powders. Using of aluminum powders has a number of advantages, such as: high performance, low cost, safety in use, safety during transportation, storage, has a minimum weight, the ability to easily obtain dispersed sizes and extend the shelf life.

Poor mixing of solids components in energy systems, small contact surface areas, strong diffusion resistance make it difficult for solid-phase reactions to occur, they pass at a very slow speed and require long-term maintenance at high temperatures. Therefore, the next important direction of the doctoral dissertation is the use of the process of mechano – chemical processing (MCP) for the synthesis of highly dispersed flameless heaters. After all, it allows you to effectively manage the process of forming new structural compositions, which ensures an increase in the energy capacity of the system.

Scientific novelty of the work:

- For the first time, the Al_S-Al_F-MnO_2-SiO system for flameless heaters activated by air was obtained by mechanochemical activation, and was determined, that the maximum combustion temperature of the system is 886.4°C, the uniform combustion rate is 0.22 mm/s;

- The composite material Al-Al_2O_3-CaO-Na_2CO_3 was obtained, providing temperatures in the range of 28-55°C during the exothermic reaction, calculated thermodynamic characteristics: combustion temperature (T=859K) and enthalpy (ΔG=21140.5 kJ/mol);

- The addition of SiO_2 to the Al-Al_2O_3-CaO-Na_2CO_3 system and the mechanochemical activation of the composite material made it possible to increase the temperature of the exothermic reaction with water to 101°C. It was calculated, that the combustion temperature of the system is 2134 K, and the value of ΔH is -9947.5 kJ/mol.

The research objective of the thesis is to obtain and study new energy-efficient composites based on highly dispersed aluminum powders, calcium oxide and silicon dioxide by mechanochemical activation for flameless heaters.

The object of the study is aluminum powders obtained by mechanochemical processing and high-energy pyrotechnic dispersed powders based on magnesium and calcium.

The subject of the study is the study of the influence of mechanochemical activation on the reactivity and structural stability of composite materials for flameless burners.

To achieve the set goal, the following tasks were set:

- Development of air-activated flameless heater composites based on Al and SiO for autonomous heat sources and study of their energy and thermodynamic characteristics;

- Study of the influence of mechano-chemical treatment conditions and parameters on the reactivity of the composition of an air-activated flameless heater based on Al and SiO;

- Development of exothermic composites of water-activated flameless heaters based on calcium oxide and mechanically activated aluminum for flameless heaters for medical purposes;

- Development of a method for increasing the energy efficiency of a water-activated flameless heater based on CaO, Al by introducing SiO_2 into the composite system by mechano-chemical activation in order to expand the range of applications of the resulting composites.

Methodological base of scientific research. To conduct scientific research on the topic of the dissertation, the following modern laboratory tools and equipment were used: planetary mill "Retsch PM100", electron microscope "Pulverisette 5" Fritsch, Germany, Quanta 3D 200i, laser granulometer MALVERN MASTERSIZER 2000, for differential thermal analysis – NETZSCH 449f3a-0372-M.

Basic principles to be protected:

- Obtained air-activated composite material for a flameless heater by mechanochemical activation of the system Al_S-Al_F-MnO_2-SiO for 50 minutes, which is characterized by an Al content of 67.8%, a maximum combustion temperature of 886.4^0C and a speed of combustion 0.22mm/s.

- Determined optimal composition of the water-activated system 40% CaO-30% Al_2O_3-15% Al-15% Na_2CO_3 for flameless heaters for medical purposes, which release heat up to 55^0C, according to thermodynamic calculations, composite system gives an energy of 21140.5 kJ/mol at 859 K and in accordance with it, determined the compositions of the combustion product;

- Obtained water-activated composite material for flameless heaters for food heating purposes with adding 15% SiO_2 to the system Al-Al_2O_3-CaO-Na_2CO_3 by mechanochemical modification of 15 min, which gives a temperature of up to 101^0C, according to thermodynamic calculations, the combustion process of this system gives an energy of 9947.5 kJ/mol at temperature of 2134K.

The practical significance of the work is that on the basis of the results obtained, approaches were proposed to obtain composites for autonomous flameless heaters based on dispersed aluminum powders and their modification by mechano – chemical activation. The proposed methods can be used to replace metal impurities such as traditional magnesium, iron used in flameless heaters with a simpler and more affordable metal, as well as to improve the operational characteristics and shelf life of composites.

The personal participation of the author in obtaining the results of the dissertation consists in setting research goals, reviewing and analyzing domestic and foreign scientific and technical literature, performing a complex of experimental studies on the preparation of dispersed aluminum powders by

preliminary mechano-chemical processing, obtaining composites for flameless heaters and converting them by mechano-chemical activation. It consists in analyzing the composition and properties of the obtained composites and products, processing and summarizing the results obtained, as well as identifying ways to solve the practical and theoretical problems posed, writing articles based on the results obtained.

Publications. The main results of the dissertation work were published in 7 printed works, of which 1 article was included in the Scopus and Thomson Reuters databases, 3 publications were published in publications recommended by the committee for control in the field of Education and science of the Republic of Kazakhstan, 3 printed works were published in collections of international scientific and practical conferences and symposiums.

Approbation of the work. The results of the dissertation were reported and discussed at the following international scientific conferences:

- Materials of the conference of students and young scientists dedicated to the 30th anniversary of the Institute of combustion problems (Almaty, November 30, 2017);
- X International Symposium “Physics and chemistry of carbon and Nanoenergy materials” (Almaty, September 12-14, 2018);
- International Conference of students and young scientists “Farabi Alemi”, April 8-11, 2019, Almaty, Kazakhstan.

The structure and content of the dissertation. The dissertation work is presented on 103 pages of machine-printed text and includes 34 Figures, 22 Tables. The work consists of an introduction, a review of the literature, a description of objects and research methods, results and their discussion, a conclusion and a list of 158 sources of literature used.