ABSTRACT

of the PhD dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (PhD) in the educational program «8D07103 Chemical Technology of Explosives and Pyrotechnic Materials»
Bexultan Zhansaya Bexultanqyzy on the topic "Development of energy-intensive cumulative impact systems"

General characteristics of the work. This dissertation presents a comprehensive study aimed at developing and characterizing cumulative energy composites based on ammonium perchlorate (PA) and carboxymethyl cellulose (CMC) modified with transition metal ions. The thermal decomposition and combustion characteristics of these materials were determined, and the influence of the catalyst on the formation of the system's directional thermal and reaction-kinetic response was determined.

It was shown that the interaction of Ni^{2+} ions with CMC functional groups (–COOH, –OH) leads to the formation of stable coordination complexes and localized catalytic sites that create cumulative heat-generating regions. These structures contribute to increased thermal conductivity, improved homogeneity of the composite material, and accelerated heat transfer throughout its volume.

Thermal studies (DSC/TGA) revealed that the introduction of nickel reduces the onset temperature of decomposition of the PA/CMC composite to 345°C and increases the total mass loss to 99.1%. Nickel's catalytic activity is related to its participation in Ni^{2+}/Ni^{3+} redox transitions and the activation of perchlorate ions, which facilitates the formation of a more powerful and concentrated decomposition energy wave.

Combustion tests showed that the nickel-containing composite (PA/CMC–Ni) exhibits a more intense and stable thermal regime: the maximum flame temperature increases from 1105°C to 1207°C, and the time to reach Tmax decreases from 5.21 s to 4.38 s. An increase in the linear combustion rate was recorded at all pressure levels, while pressure sensitivity decreased (n = 0.475 versus 0.499 for the unmodified composite), indicating process stabilization and increased efficiency of the cumulative thermal effect.

Relevance of the research topic. Research in the field of solid rocket propellants remains highly relevant due to the growing demands for reliability, energy efficiency, and environmental safety of modern rocket, space, and defense systems. Solid rocket propellants are a key component for a wide range of aircraft—from space launch vehicles and satellite platforms to tactical missile systems—making improving their composition and characteristics a strategically important task.

The global trend toward miniaturization of rocket and spacecraft requires the development of more efficient propellants with increased energy density, improved thermal stability, and the ability to accurately predict combustion parameters. This ensures increased thrust performance while reducing the weight of rocket systems.

Technical requirements for the safe operation and storage of propellants are stimulating the development of less sensitive and more stable composites. Increased resistance to external influences, a reduced risk of spontaneous decomposition, and predictability of behavior over a wide temperature range are critical factors for practical applications.

The rapid development of additive manufacturing technologies, the use of catalysts, flame retardants, nanomaterials, and functional binders are opening up new avenues for research. Modifying composite matrices, implementing highly efficient catalysts, improving heat transfer, and controlling microstructure are enabling advances toward the creation of "smart" fuels with controlled combustion characteristics.

Finally, research in the field of TRT is highly significant for the development of national and international space infrastructure.

Purpose of the work. The purpose of this dissertation is to develop and study cumulative-type composite energy-intensive materials based on PA and CMC modified with transition metals, and to establish the patterns of their thermal decomposition, combustion, and the catalytic effect of metal ions on energy release processes.

Objectives of the work. To achieve this goal, the following objectives were set in this dissertation:

1. To investigate the formation mechanisms of CMC-based polymer matrices doped with transition metal nanoparticles and to identify the role of Ni–O–C coordination bonds in providing controlled heat generation.
2. To establish the effect of nickel-modified PA/CMC–Ni structures on the formation of active zones of cumulative catalytic action and determine how Ni–O–C units accelerate thermal decomposition processes based on the physicochemical characteristics of the resulting composites.
3. To analyze the effect of Ni coordination centers on the thermal dynamics of stable combustion of PA/CMC and to determine the mechanisms for enhancing the thermal regime during thermal decomposition using DSC, DTG, and TGA. 4. Develop and substantiate methodological principles for modifying CMCs of transition metal ions, ensuring controlled formation of cumulative heat-affected zones in energy-intensive composite systems, and determine their role as a technical basis for designing materials with a directed and predictable thermal response.

Key points to be defended:

1. Polymer matrices based on CMC and transition metal compounds with Ni–O–C coordination bond types provide controlled heat release with energy Eb = 850–866 eV and form a cumulative thermal response in energy-intensive composites at K≈1.8–1.9
2. Nickel-modified PA/CMC–Ni composites with active zones of cumulative catalytic action accelerate the decomposition of energy-intensive

components to 31°C due to the formation of Ni–O–C units at ΔT = 376 °C to 345 °C with a mass loss of up to 99.1% at a maximum energy density of the system ENipl≈1.64 kJ/g

3. Ni coordination centers enhance the thermal dynamics of combustion of energy-intensive systems from 1105 °C to 1207 °C at An effective thermal acceleration coefficient of Kacceleration≈1.20 with a reduction in the time to reach the temperature maximum to ~1 second.

4. The methodology for modifying CMCs with transition metals ensures the controlled formation of cumulative heat-affected zones in energy-intensive systems and provides a technical basis for designing energy-intensive composites with a targeted and predictable thermal response in thermally active energy-intensive fuels.

Research Object. The research object is cumulative-type composite energy materials consisting of PA as an oxidizer and CMC as an organic binder, modified with transition metal ions (Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}).

Research Subject. The research subject is the fundamental principles of optimizing the combustion characteristics of ammonium perchlorate-based composites using carboxymethyl cellulose doped with transition metal oxides.
To experimentally evaluate the performance of the developed TRPs, laboratory combustion experiments were conducted on samples at various initial pressures (1-10 MPa) to determine the combustion rate and the pressure exponent affecting the safe performance of the TRPs.

Research Methods. The morphology and structural properties of the resulting materials were studied using SEM/EDS, X-ray diffraction, XPS, IR, and Raman spectroscopy. Kinetic studies were conducted using differential thermal analysis (DTA). DTA combines several research methods, including differential scanning calorimetry (DSC), differential thermogravimetry (DTG), and thermogravimetric analysis (TGA).

Scientific Novelty of the Study:

1. For the first time, patterns of Ni–O–C thermal energy redistribution in the CMC polymer matrix have been established, providing controlled heat release with characteristic energy parameters (Eb = 850–866 eV).

2. The catalytic effect of Ni–O–C zones in PA/CMC–Ni composites has been revealed, leading to accelerated thermal degradation of energy-intensive components from 376°C to 345°C, demonstrating a new mechanism for the influence of metal–polymer coordination units on thermal processes.

3. For the first time, an enhancement of the thermal dynamics of combustion under the influence of Ni coordination centers has been established, leading to an increase in the maximum flame temperature to 1207°C and a reduction in the time to reach the temperature maximum to ~1 second. This allows us to consider such centers as active modulators of the thermal regime of high-energy systems.

4. A set of methodological principles for modifying CMC with transition metal ions has been developed, ensuring the controlled formation of cumulative heat-affected zones and creating a scientific basis for the design of energy-intensive composites with a predictable and directional thermal response.

Theoretical Significance. Scientifically substantiated criteria for selecting chemical compositions with marking properties are presented. Methods for introducing marking additives into explosive compositions and their subsequent identification are established. The absence of a negative impact of marking additives on the performance characteristics of explosives, including their safe use, is confirmed.

The obtained thermokinetic data provide insight into the transformations that occurred, such as phase transitions, decomposition, melting, kinetics, and thermal stability of the developed TRTs.

The established degree of catalytic activity of the catalysts theoretically describes the PA decomposition model depending on the catalyst type. Studying gaseous and condensed combustion and decomposition products determines the mechanism of chemical transformation of energy-intensive compounds and the degree of influence of CMCs with various transition metals on the combustion efficiency of solid propellant fuel.

Practical Significance. The Republic of Kazakhstan possesses one of the best cosmodromes, Baikonur, and has the potential to attract investment interest from investors for the implementation of international space programs, as evidenced by the "Kazakhstan-2050" space reform strategy. The new Kazakhstan requires new projects and qualified personnel for fruitful scientific research at the international level in this field.

Thesis approval. The results of this dissertation were presented and discussed at the following international and national scientific and technical conferences and symposia:

1. Zhansaya Beksultan, Marat Nurguzhin, Marat Janikeyev, Myrzakhan Omarbayev, Azira Yermakhanova, Mohammed Meiirbekov, Miras Zhumakhanov, Aidos Lesbayev, Darkhan Yerezhep, Meiram Atamanov, Marat Tulepov, Optimizing Combustion Characteristics of Ammonium Perchlorate Composites with Nickel-Enhanced Carboxymethyl Cellulose. Aerospace. 2025, 12(4), 270; https://doi.org/10.3390/aerospace12040270

2. Marat Tulepov, Larissa Sassykova, Dauren Baiseitov, Bibigul Rakhimova , Fedosya Abdrakova , Galiya Spanova, Sestager Aknazarov, Zhansaya Beksultan Synthesis and optimization of combustion of briquettes based on substandard brown coals of Kazakhstan deposits with multipolymer binders Mediterranean Journal of Chemistry 2020, 10(3), 302-309 DOI:10.13171/mjc02003271253ls

3. Ж.Б. Бексултан, М.И. Тулепов, М.К. Атаманов, Разработка эластичного кумулятивного заряда на основе гелеобразующих веществ, Горение и плазмохимия. -2020.-№3. – С. 132-140 DOI: https://doi.org/10.18321/cpc361

4. F.Yu. Abdrakova, M.I. Tulepov, D.A. Baiseitov Zh.B. Beksultan, M. Chikhradze Localization of explosion pulses in a closed space in coal mines Горение и Плазмохимия 19 (2021) 131-138 https://doi.org/10.18321/cpc426

5. М.И. Тулепов, Ж. Бексултан, Ш.Е. Габдрашова, Д.А. Байсейтов, И.А. Пустовалов, С. Алешкова Экспериментальное определение показателей безопасности эмульсионных взрывчатых веществ, содержащих в качестве

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6. Тулепов М.И., Бексултан Ж.Б. Разработка энергоемких систем кумулятивного воздействия "Химические проблемы современности" г. Донецк, 19-21 мая 2020г.

7. Ж.Б.Бексултан, М.И. Тулепов, М.К.Атаманов, Ш.Т. Султахан, Приготовление карбоксиметилцеллюлозы, допированной оксидами переходных металлов для эффективного сгорания топлива на основе перхлората аммония “Химиялық физика және наноматериалдар” атты VII Жас Ғалымдар Конференциясының Еңбектер Жинағы, 2020г.

9. Ж.Б.Бексултан, М.И. Тулепов, М.К.Атаманов, Энергетические конденсированные системы, Монография Белая книга по энергоемким материалам. Алматы ТОО «Издательство Дарын». -224.- 264 с.

10. Bexultan Zh.B., Korchagin M.A., Sassykova L.R., Abdrakova F.Y., Aitenov Y.K., Toktagul S.E., Baiseitov D.A. Gabdrashova S.E., Development of pyrotechnic delay mixtures based on a composite material hardened with carbon nanotubes. Digest Journal of Nanomaterials and Biostructures. 2021. V. 16, Iss. 4, P 1341 – 1350. DOI:10.15251/DJNB.2021.164.1341

11. Ж.Б.Бексултан, М.И. Тулепов, М.К.Атаманов, Разработка эластичного кумулятивного заряда на основе гелеобразующих веществ сборник трудов международного казахстанско-российского симпозиума «Химическая физика и наноматериалы», Казахстан, издательство: «Қазақ университеті» 2021г.

Author's Personal Contribution. The author's personal contribution includes setting up and conducting experiments, summarizing and interpreting the results, and writing articles and reports. The purpose and objectives, experimental planning, discussion of results, and key points for the defense were discussed with both scientific advisors.

Publications. The main results of this dissertation were published in 11 publications, including one article included in the Web of Science database, three publications in journals recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Higher Education of the Republic

of Kazakhstan, one monograph, and six in proceedings of international symposia and international conferences.

Relationship with research projects and government programs. The dissertation submitted for defense, "Development of Energy-Intensive Cumulative Impact Systems," was developed at the author's initiative.

Scope and Structure of the Dissertation. The dissertation is 115 pages long and includes 47 figures and 14 tables. It consists of an introduction, literature review, description of the objects and methods of study, results and their discussion, conclusion, and a list of 149 references.