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Editorial

Advanced Energetic Materials: Testing and Modeling

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Energetic Materials (EMs) are a traditional branch of materials. It started more than 2000 years ago in China with black powder, or something very close to it. In recent years, the demand for industrial and defense applications for energetic materials, including pyrotechnics, explosives, and propellants, inspired new developments in this field. The occurrence of advanced energetic materials in particular offers a unique new opportunity to improve the performance of energetic formulations. DB propellants, as homogeneous mixtures of NC (nitrocellulose) with NG (nitroglycerin), have been widely applied to solid rocket propulsion. The composite modified double base (CMDB) propellant, often used in military missiles and space vehicles, properly combines specific features of the two previous kinds of propellant. They are smokeless and are suitable for free standing motor grain configurations thanks to their high strength and elastic modulus. Composite propellants are a multi-phase mixture of oxidizing particles (such as AP) and metal fuel particles (such as Al) with high polymers as the matrix. For example, hydroxyl-terminated polybutadiene (HTPB) is a polymer widely used in propulsion both for composite solid propellants and hybrid fuels. As a typical composite propellant, high-energy HTPB propellant has the advantages of excellent combustion performance and mechanical properties, low flame temperature, low molecular combustion products, and low infrared radiation. However, it also has a high probability of detonation and the risk of detonation. Today, an important challenge concerns the solid oxidizers and insensitive compositions. On top of the energetic performance, large density, low-cost, low-sensitivity to multiple stimuli, low characteristic signature, slow aging, reliable safety, green features before and after burning, easy disposal, and reuse technology are also of great interest to researchers and users of solid propellants. Innovative energetic materials, such as DNTF, RDX@FOX composite, and so on, are often incorporated into propellant composition and require attention. When they were introduced to the energetic system, the performance of the system would be influenced significantly. It is critical to fully consider the properties of both the material and the composite system when selecting the cladding material to ensure that the propellant energy, ignition, density, and other characteristics are maintained while effectively improving the crystallization of DNTF and maintaining stable control of its crystallization amount. Recently, the emergence of high-energy density compounds, such as CL-20, 3,4-Bis(3-nitrofurazan-4-yl) furozan (DNTF), and Ni/Al energetic structural materials, allowed formulating new propellants with an increased energy density. Thus, high-energy, low vulnerability, and green solid propellants, laser-driven combustion, etc., are now hot topics worldwide. Moreover, with the development of computer science and technology, many theoretical simulation methods, such as molecular dynamics simulation, artificial neural networks (ANN), nonlinear dynamics software LS-DYNA, etc., can be used to investigate the performance of EMs. For example, the high-energy materials genome (HEMG) is based on the experimental data on the combustion and detonation characteristics of various high-energy materials (HEMs)

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under various conditions, being based also on the metadata on the quantum and physicochemical characteristics of HEMs components as well as the thermodynamic characteristics of HEM as a whole.

To accelerate the potential applications, various works focused on the physical and chemical characteristics through theory, experiments, and simulations. The aim of this issue is to collect comprehensive knowledge on materials synthesis, characterization, combustion, mechanical, detonation, and safety. This Special Issue *Advanced Energetic Materials: Testing and Modeling* explores innovative EMs and EMs ingredients as well as formulations test and models. It collected contributions covering recent progress and models of energetic materials in chemical propulsion. Attention was focused on the design, model, properties, and state of-the-art of this class of thermochemical propulsion devices. A total of 13 papers were selected for publication after a standard peer review process, which summarize the most recent achievements of famous research groups, participation of young authors with novel/innovative concepts was especially encouraged, of course, with the assistance of their supervisors.

To investigate the crystallization of DNTF in modified double-base propellants, glycidyl azide polymer (GAP) was used as the coating material for the in situ coating of DNTF, and the performance of the coating was investigated to inhibit the crystallization. Molecular dynamics was used to construct a bilayer interface model of GAP and DNTF with different growth crystal surfaces, and molecular dynamics' calculations of the binding energy and mechanical properties of the composite system were carried out by Qin, Y. [1]. It was found that GAP can form a white gel on the surface of DNTF crystals and has a good coating effect which can significantly reduce the impact sensitivity and friction sensitivity of DNTF. GAP could effectively improve the mechanical properties of DNTF. GAP can be referred to as a better cladding layer for DNTF, which is feasible for inhibiting the DNTF crystallization problem in propellants.

In order to study the ignition process and response characteristics of cast polymer-bonded explosives (PBXs) under the action of friction, HMX-based cast PBXs were used to carry out friction ignition experiments at a 90° swing angle and obtain the critical ignition loading pressure was 3.7 MPa. The friction temperature rise process was numerically simulated at the macro and micro scale, and the ignition characteristics were judged by Yuan, J. [2]. It was found that the maximum temperature rise was 55 °C, and the temperature rise of the whole tablet was not enough to ignite the explosive. HMX crystal particles can be ignited at a temperature of 619 K under 4 MPa hydraulic pressure loaded by friction sensitivity instrument. The external friction heat between cast PBX tablet and sliding column had little effect on ignition.

To study the engine safety against fragment in complex battlefield environments, the fragment impact safety simulation study of a high-energy four-component HTPB propellant solid engine was conducted. The equation of state parameters and reaction rate equation parameters of the detonation product of HTPB propellant were calibrated by using a 50 mm diameter cylinder test and Lagrange test combined with genetic algorithm. The nonlinear dynamics software LS-DYNA was used to build a finite element model of the fragment impact engine and simulate the mechanical response of the high-energy HTPB propellant under different operating conditions by Liu, Z. [3]. It was found that the critical detonation velocity decreased with the increase in the number of fragments. When the number of fragments was more than five, the influence of this factor on the critical detonation velocity was no longer obvious. Under the same loading strength conditions, the greater the metal shell strength and the greater the shell wall thickness, the more difficult it was for the HTPB propellant to be detonated by the shock. This study can provide a reference for the design and optimization analysis of solid rocket engine fragment impact safety.

For the solid propellant burning rate prediction, high-energy materials genome (HEMG) is an analytical and calculation tool that contains relationships between variables of the object, which allows researchers to calculate the values of one part of the variables through others, solve direct and inverse tasks, predict the characteristics of non-

experimental objects, predict parameters to obtain an object with desired characteristics, and execute virtual experiments for conditions which cannot be organized or have difficultly being organized. The history and current status of the emergence of HEMG are presented herein. The fundamental basis of the artificial neural networks (ANN) as a methodological HEMG base, as well as some examples of HEMG conception used to create multifactor computational models (MCM) of solid rocket propellants (SRP) combustion, was presented by Pang, W. [4].

To study the role of complex composition of 2:17R-cell boundaries in the realization of magnetization reversal processes of (Sm, Zr)(Co, Cu, Fe)$_z$ alloys intended for high-energy permanent magnets, the micromagnetic simulation was performed using the modified sandwich model of a (Sm, Zr)(Co, Cu, Fe)$_z$ magnet, which includes additional domain-wall pinning barriers in the form of 2:7R or 5:19R phase layers by Zheleznyi, M. [5]. It was found that there was a possibility of reaching the increased coercivity at the expense of 180°-domain wall pinning at the additional barriers within cell boundaries. The phase and structural states of the as-cast $Sm_{1-x}Zr_x(Co_{0.702}Cu_{0.088}Fe_{0.210})_z$ alloy sample with $x = 0.13$ and $z = 6.4$ were studied, and the presence of the above phases in the vicinity of the 1:5H phase was demonstrated.

Research on energetic materials continuously develops energetic materials with higher detonation performance and energy density, taking it as an eternal quest. Due to the introduction of oxygen atoms, N-oxide energetic compounds have a unique oxygen balance, excellent detonation properties, and a high energy density, attracting the extensive attention of researchers all over the world. Synthetic strategies towards azine N-oxides and azole N-oxides of N-oxides were fully reviewed. Corresponding reaction mechanisms towards the aromatic N-oxide frameworks and examples that use the frameworks to create high-energy substances were discussed. Moreover, the energetic properties of N-oxide energetic compounds were compared and summarized by She, W. [6].

As we know, aluminum (Al) has been widely used in micro-electromechanical systems (MEMS), polymer-bonded explosives (PBXs), and solid propellants. Its typical core–shell structure (the inside active Al core and the external alumina (Al_2O_3) shell) determines its oxidation process, which is mainly influenced by oxidant diffusion, Al_2O_3 crystal transformation and melt-dispersion of the inside active Al. Metastable intermixed composites (MICs), flake Al, and nano Al can improve the properties of Al by increasing the diffusion efficiency of the oxidant. Fluorine, titanium carbide (TiC), and alloy can crack the Al_2O_3 shell to improve the properties of Al. Furthermore, those materials with good thermal conductivity can increase the heat transferred to the internal active Al, which can also improve the reactivity of Al. The integration of different modification methods was employed by Wang, D.to further improve the properties of Al [7]. With the ever-increasing demands on the performance of MEMS, PBXs, and solid propellants, Al-based composite materials with high stability during storage and transportation, and high reactivity for usage will become a new research focus in the future.

It is difficult for the reactor to achieve uniform quality of composite material, which affects its application performance. 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,1-diamino-2,2-dinitroethylene (FOX-7) are famous high-energy and insensitive explosives. The preparation of RDX@FOX-7 composites can meet the requirements with high-energy and low sensitivity. Based on the principle of solvent-anti-solvent, the recrystallization process was precisely controlled by microfluidic technology. The RDX@FOX-7 composites with different mass ratios were prepared by Yu, J. [8]. It was found that at the mass ratio of 10%, the RDX@FOX-7 composites were ellipsoid of about 15 μm with uniform distribution and quality. The advantages of microscale fabrication of composite materials were verified. With the increase in FOX-7 mass ratios, the melting temperature of RDX was advanced, the thermal decomposition peak of RDX changed to double peaks, and the activation energy of RDX@FOX-7 composite decreased. These changes were more pronounced between 3 and 10%, but not between 10 and 30%. The ignition delay time of RDX@FOX-7 was shorter than

that of RDX and FOX-7. RDX@FOX-7 burned more completely than RDX indicating that FOX-7 can assist heat transfer and improve the combustion efficiency of RDX.

Ni/Al energetic structural materials attracted much attention due to their high energy release, but understanding their thermal reaction behavior and mechanism in order to guide their practical application is still a challenge. A novel understanding of the thermal reaction behavior and mechanism of Ni/Al energetic structural materials in the inert atmosphere were reported. The reaction kinetic model of Ni/Al energetic structural materials with Ni/Al molar ratios was obtained. The effect of the Ni/Al molar ratios on their thermal reactions was discussed based on the products of a Ni/Al thermal reaction by Wang, K. [9]. It was found that the liquid Al was adsorbed on the surface of Ni with high contact areas, leading in an aggravated thermal reaction of Ni/Al.

Taking the combustion tear gas mixture as the research object, the system formula was optimized by adding a different mass fraction of 5-amino-1H-tetrazole (5AT). TG-DSC, a thermocouple, and a laser smoke test system were used to characterize the combustion temperature and velocity, as well as the smoke concentration and particle size. Starink's method, the Flynn–Wall–Ozawa method, and the Coats–Redfern method were used to evaluate the pyrolysis kinetic parameters of the samples by Zhai, H. [10]. It was found that when the mass fraction of 5AT in the system was 10%, the maximum combustion temperature of the sample decreased by nearly 70 °C and the smoke concentration increased by 12.81%. Adding an appropriate amount of the combustible agent 5AT to the combustion tear gas mixture can improve its combustion performance and smoking performance, which provides an important, new idea for the development of a new generation of safe, efficient, and environmentally friendly tear gas mixtures.

To study the design method and pressure relief effect of the mitigation structure of a shell under the action of thermal stimulation, a systematic research method of theoretical calculation-simulation-experimental verification of the mitigation structure was established by Liang, J. [11]. The pressure relief effect of the mitigation structure was verified by the low-melting alloy plug with refined crystal structure for sealing the pressure relief hole and the cook-off test. It was found that the critical pressure relief area is when the ratio of the area of the pressure relief hole to the surface area of the charge is $A_V/S_B = 0.0189$. When the number of openings increased to 6, the required pressure relief coefficient decreased to $A_V/S_B = 0.0110$. When the length/diameter ratio was greater than 5, the opening at one end cannot satisfy the reliable pressure relief of the shell. The designed low-melting-point alloy mitigation structure can form an effective pressure relief channel.

To study the crystal mechanical properties of DNTF and hexanitrohexaazaisowurtzitane (CL-20) deeply, the crystals of DNTF and CL-20 were prepared by the solvent evaporation method. The crystal micromechanical loading procedure was characterized by the nanoindentation method. In addition, the crystal fracture behaviors were investigated with scanning probe microscopy (SPM) by Nan, H. [12]. It was found that the hardness for DNTF and CL-20 was 0.57 GPa and 0.84 GPa, and the elastic modulus was 10.34 GPa and 20.30 GPa, respectively. CL-20 obviously exhibited a higher hardness, elastic modulus, and local energy-dissipation, and a smaller elastic recovery ability of crystals than those of DNTF. CL-20 crystals are more prone to cracking and have a lower fracture toughness value than DNTF. Compared to DNTF crystals, CL-20 is a kind of brittle material with higher modulus, hardness, and sensitivity than that of DNTF, making the ignition response more likely to happen.

In order to study the reaction growth process of insensitive Ju En Ao Lv (JEOL) explosive after ignition under cook-off, a series of cook-off tests were carried out on JEOL explosive using a self-designed small cook-off bomb system. A thermocouple was used to measure the internal temperature of the explosive, and a camera recorded macro images of the cook-off process by Wang, X. [13]. It was found that the ignition time decreased as the heating rate increased, while the ignition temperature was not sensitive to the heating rate. When the heating rate was faster, the internal temperature gradient of the explosive was larger, and the ignition point appeared at the highest temperature position. As the heating

rate decreased, the internal temperature gradient of the explosive decreased, the ignition point appeared random, and multiple ignition points appeared at the same time. The growth process of the ignition point could be divided into severe thermal decomposition, slow combustion, and violent combustion stages.

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