Preparation of Energetic Composites Materials via Sol-Gel

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Abstract. In this research, nitrocellulose / magnesium borohydride nanomaterials (NC / Mg(BH₄)ₓ) nanoenergetic composite materials are synthesized through sol-gel method and the freeze-drying technology. Among them, nitrocellulose (NC) is used as a gel matrix to load Mg(BH₄)ₓ particles. Scanning electron microscopy (SEM) results show that Mg(BH₄)ₓ is embedded and uniformly dispersed in the NC matrix. The particle size of the high-energy composite material is about 2 μm. The results of FT-IR showed that the hydrogen storage alloy was successfully loaded around the NC without destroying the cellulose structure. The composite material decomposition reaction (Temperature-Time) curve is obtained through the adiabatic accelerated calorimeter (ES-ARC) test.

1. Introduction

Hydrogen is attracting more and more attention because of its abundant reserves, high energy density, and clean green new energy. However, the transportation, storage and use of hydrogen require special conditions such as low temperature and high pressure, and its technology is more complicated, costly and unsafe[1]. Therefore, to introduce hydrogen energy into energetic materials such as explosives and solid propellants, the use of safe and reliable high-capacity hydrogen storage materials is currently one of the most feasible methods[2]. The combustion of solid propellant is a redox process with a faster reaction rate, which requires the hydrogen storage material in it to release H₂ at a faster rate. The application in solid propellants puts forward higher requirements on the thermodynamic and kinetic properties of hydrogen storage materials. If the thermodynamic and kinetic properties of hydrogen storage materials do not meet the requirements, the stored hydrogen cannot be promoted. When the propellant is burned, it will be converted into hydrogen in time, and will participate in the combustion of the propellant in other ways, which is contrary to the original intention of introducing hydrogen storage materials into the propellant, and is not conducive to the improvement of the specific impulse of the propellant[3]. Nanometerization can shorten the mass transfer path of hydrogen release reaction of hydrogen storage materials and improve the kinetic performance; at the same time, nanometerization can significantly increase the specific surface area of the material, increase the surface energy of the material, and decrease the nucleation activation energy, thereby reducing The energy barrier for the hydrogen-release reaction of hydrogen storage materials[4]. The mixing of components on the nano- or sub-micron scale can increase the energy release rate and reduce the sensitivity[5]. The sol-gel processes allow fuels to be mixed on the nanometer scale to control the component size and distribution through the final drying process. The presence of the gel matrix effectively prevents the agglomeration of particles, controls the particle size at the nanometer level, reduces the sensitivity of hydrogen storage materials, and improves energy and combustion performance.
Therefore, in this study, aluminum isopropoxide was used as a crosslinking agent, nitrocellulose was used as a high-energy gel matrix, and the hydrogen storage alloy Mg(BH$_x$)$_y$ was loaded in the gel matrix to prepare NC / Mg(BH$_x$)$_y$ composite containing Energy materials, due to the cross-linked structure of the gel matrix, the sensitivity is significantly reduced, and the cross-linked structure can act as a buffer system to reduce the stimulus release from the surrounding environment.

2. Materials and methods

2.1. Materials
NC(11.88% N), China North Chemical Industry Group Co., Ltd; Mg(BH$_x$)$_y$, provided by Shanghai Jiao Tong University; Acetone(AR), Sinopharm Chemical Reagent Co., Ltd.; Aluminum isopropoxide (AR), Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2. Preparation of NC / Mg(BH$_x$)$_y$
Dry the nitrocellulose raw material to a constant weight for use. Dissolve 0.6g NC in 10ml acetone under magnetic stirring, and stir for 20min. 0.4g of Mg(BH$_x$)$_y$ was added to the nitrocellulose solution, stirred for 4h and sonicated to obtain a uniform solution, the aluminum isopropoxide crosslinker solution was quickly added to the solution for mixing, and the solution was quickly crosslinked into a gel. Finally, the gel is instantaneously frozen with liquid nitrogen, and then dried by vacuum freeze-drying technology. The drying conditions are precisely controlled through extremely low temperature and vacuum (-76°C and 10-3 mbar) to ensure the safety of the experiment. The sample is named NC / Mg(BH$_x$)$_y$.

3. Results and discussion

3.1. Characterization of NC / Mg(BH$_x$)$_y$
FT-IR spectroscopy was carried out to clarify the structural characteristics of NC, Mg(BH$_x$)$_y$ and NC/Mg(BH$_x$)$_y$ composites. The results are shown in Figure 1.

![Infrared spectra of NC, Mg(BH$_x$)$_y$ and NC / Mg(BH$_x$)$_y$ composites](image)

Figure 1 Infrared spectra of NC, Mg(BH$_x$)$_y$ and NC / Mg(BH$_x$)$_y$ composites

It can be seen from Figure 1 that the nitrate stretching vibration absorption peaks of the composite material at 1637 and 1271 cm$^{-1}$ have no significant changes compared with pure NC. The C-O bond stretching vibration absorption peaks at 1067 and 987 cm$^{-1}$ are weakened. The stretching vibration
absorption peaks of methylene and methine are at 3034–2840 cm⁻¹, and the peak area of the composite material decreases. The characteristic peak intensity decreases, which indicates that the hydroxyl groups on the nitrocellulose react with the cross-linking agent.

The scanning electron microscope (SEM) images of NC, Mg(BH₃)ₓ, and NC / Mg(BH₃)ₓ composites are shown in Figure 2. It can be seen from Figure 2 that the diameter of NC is about 20 μm, the particle size of Mg(BH₃)ₓ is about 1 μm, agglomeration occurs after gelation, and the shape is irregular. The particle size of the composite material is about 2 μm, which is not observed. The fibrous structure of nitrocellulose is mainly the result of dissolving nitrocellulose in acetone.

3.2. Thermal decomposition properties of composite materials

In this study, a thermal analysis device from THT was used. The rapid adiabatic acceleration calorimeter (ES-ARC) is the heating module of the device. The operating temperature range is 25°C to 500°C, the pressure range is 0-20 MPa, and the maximum measurable sample is 15 grams. After exploring the experimental conditions, the setting temperature range is 100 ~ 250 °C, and the heating rate is 5.00 K/min. The amount of the test sample is about 20 mg to avoid serious damage to the equipment due to the high energy released. The decomposition reaction curve of the composite material sample obtained by ES-ARC is shown in Figure 3. It can be seen from Figure 4 that the exothermic peak of the composite material is relatively gentle, and the sample decomposition temperature ranges from 165 to 168°C. Compared with pure Mg(BH₃)ₓ, the decomposition temperature is advanced. The main reason is that Mg(BH₃)ₓ is a negative oxygen system. After being compounded with NC, NC can provide oxygen to the composite material and advance the decomposition reaction temperature.

![Figure 2 SEM images of NC, Mg(BH₃)ₓ, and NC / Mg(BH₃)ₓ composites](image)

![Figure 3 Decomposition reaction curve of NC / Mg(BH₃)ₓ composite](image)
4. Conclusions
In this study, NC / Mg(BH₄)ₓ composite energetic materials were prepared by the sol-gel method, and the FT-IR and XRD characterization showed that the composite did not destroy the structure of NC. The SEM image results show that the particle size of the composite material is about 2 μm.

The decomposition temperature of the composite material can be obtained from the ES-ARC test in the range of 165~168°C, and NC supplies oxygen to the energetic system, so that the composite material has an earlier decomposition reaction temperature than pure Mg(BH₄)ₓ and can increase wider its scope of application. This fabrication strategy and conclusions will provide promising application for NC / Mg(BH₄)ₓ used in propellants.

Acknowledgments
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References
[1] Nijkamp M, Raaymakers J, Van Dillen A. (2001) Hydrogen storage using physisorption–materials demands. J. Applied Physics A., 72(5): 619-623.
[2] Ji D, Wei X, Du P. (2018) Effect of Boron-Containing Hydrogen-Storage-Alloy (Mg(BH₄)ₓ) on Thermal Decomposition Behavior and Thermal Hazards of Nitrate Explosives. J. Propellants, Explosives, Pyrotechnics., 43(4): 413-419.
[3] Yanmeng D, Yunjun L, Guoping L. (2012) Thermal decomposition properties of Hydrogen storage alloy / AP / HTPB. J. Chinese Journal of Explosives & Propellants., 35(03): 66-70.
[4] Yanjing Y, Fengqi Z, Jianhua Y. (2016) Research progress in the application of nano-hydrogen storage materials in propellants. J. Chinese Journal of Energetic Materials., 24(2): 194-201.
[5] Jin M, Wang G, Deng J. (2015) Preparation and properties of NC / RDX / AP nano-composite energetic materials by the sol-–gel method. J. Journal of Sol-Gel Science&Technology., 76, 58-65