Conference Paper

Preparation and Properties of Boron-Based Nano-B/CuO Thermite

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Abstract

We adopt precipitation to prepare the nanometer CuO and coat it on boron particles of micro- and nano-size. The morphology and coating result of B/CuO nanocomposite thermite were characterized using different techniques, such as scanning electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy. The results indicated that the boron particles were coated completely by nanocomposite CuO and well distributed. The B/CuO nanocomposite thermite reaction process was tested by thermogravimetric/differential scanning calorimetry. The obtained reaction temperature of B/CuO particles is about 116.86° lower than that of boron particles. The B/CuO thermite and boron powder were added to Mg/PTFE propellant to be measured for their respective combustion performance. The results showed that the B/CuO-Mg/PTFE propellant burning rate increased by 12.87%, mass burning rate by 13.48%, and combustion temperature increased by 56.3° compared to the B-Mg/PTFE propellant. The above results indicate that the CuO coating of boron particles increases the combustion performance of propellant compared with uncoated particles.

Keywords: boron particles, thermite, propellant

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1. Introduction

In order to increase the exothermic heat of reaction, many kinds of metal components are added into the formula of energetic materials, such as magnesium, aluminum, and boron. Compared with magnesium and aluminum, boron can release more heat after complete burning. However, challenges in ignition and self-propagation of the front lead to the inefficient release of the heat in a limited time [1]. The ignition and reaction processes of boron particles have been extensively studied [2]. Boron is considered to be an attractive high-energy metallic fuel for using as a fuel-rich composition because of its high gravimetric (58.28MJ.kg^{-1}) and volumetric (136.38 kJ.cm^{-3}) caloric value during reaction with oxygen [3]. Liu [4] has studied LiF, fluororubber, and silane coated boron powder and the influence of the coating materials on the ignition and burning performances of rich-fuel composition. The results showed that LiF had the best influence on the boron-based compositions, because the reaction between LiF and B_2O_3 led to the B_2O_3 layer breaking, so the ignition property improved. Viton A can produce HF, and HF can react with B_2O_3 to produce two kinds of gases (BOF, BF_3). The B_2O_3 layer can also be cleaned in such a way. The surface and processing properties of composition were improved by coating silane. These experiments concentrated on the modified boron powder, but there are few tests about boron-based nano-system. There are

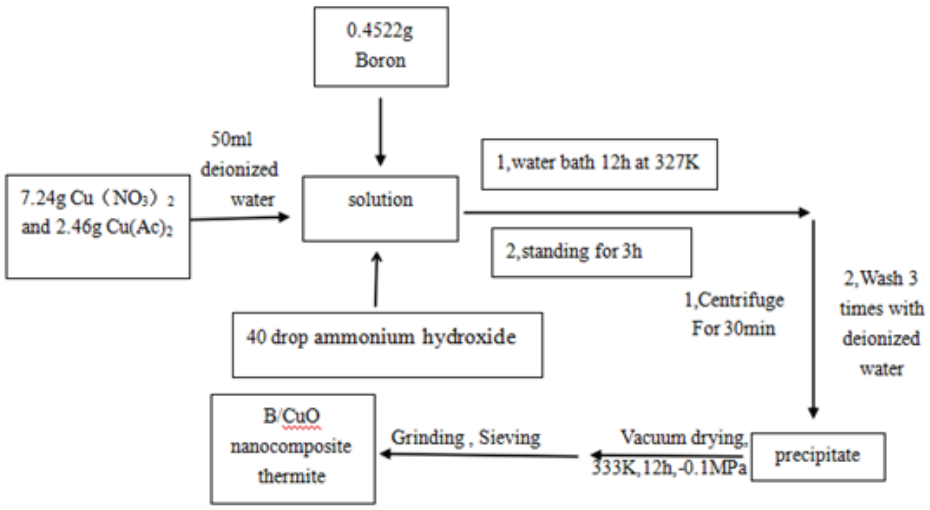

Figure 1: The preparation method of B/CuO nanocomposite thermite.

many kinds of nano-system, but most of them are Al-based, such as Al/CuO, Al/WO_3, Al/Cr_2O_3, and so on. The boron particle replaces aluminum one as the reducing agent. Sulliand [5] has studied the reaction of nano-B/Al/CuO metastable state composites. When the contents of nano-boron particle reach the 50% of fuels, nano-Al/CuO can increase the reaction property of nano-boron. And when the grain size of boron particle reached 700 nm, the efficiency was obvious.

As particles are reduced from a micrometer to a nanometer size, the resultant properties can change dramatically. For example, electrical conductivity, hardness, active surface area, chemical reactivity, and biological activity are all known to be altered [6]. There are many methods to prepare nano-CuO, such as precipitation method, hydrothermal method, solid phase method, and so on [7]. The article discusses the precipitation method to prepare nano-B/CuO and test the properties of nanocomposite thermite by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and thermogravimetric/differential scanning calorimetry (TG-DSC).

2. Experiment

The used raw materials are shown in Table 1. The preparation processes of B/CuO nanocomposite thermite and B-Mg/PTFE and B/CuO-Mg/PTFE propellant grains are indicated in Figures 1 and 2, respectively.

The boron particle size distribution was examined with the Laser Particle Analyzer (BT9300H, Dandong Bettersize Instruments Ltd). The morphology of boron and B/CuO nanocomposite thermite particles was observed with field emission scanning electron microscopy (QUANTA, FEG250, FEI Company; S-4800, Hitachi Limited). The elements of boron powder and B/CuO nanocomposite thermite were examined with energy disperse spectroscopy (4473C-1UUS-SN, Thermo Fisher Scientific). The EDS was linked

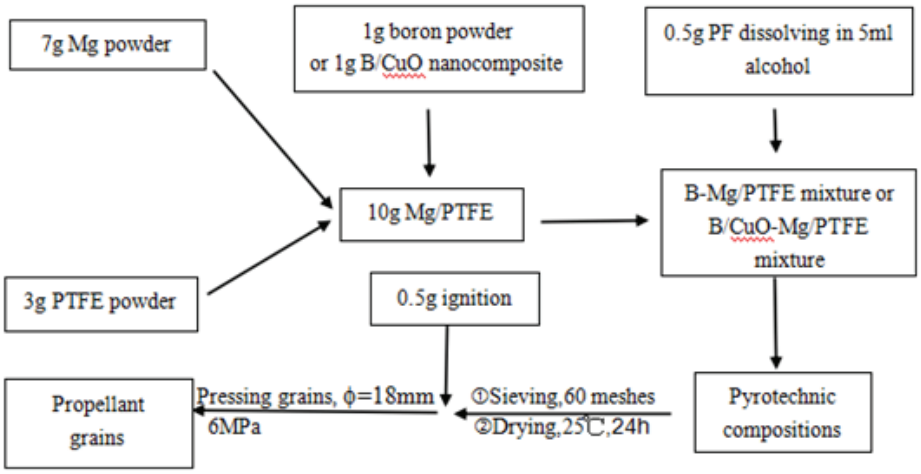

Figure 2: The preparation process of propellant grains.

Reagent	Chemical formula	The purity or particle size	Manufacture
Copper nitrate trihydrate	$Cu(NO)_3 \cdot 3H_2O$	A.R,purity99.5%	Sinopharm Chemical Reagent.Co.,Ltd
Copper acetate hydrate	$Cu(CH_3COO)_2 \cdot H_2O$	A.R,purity99.5%	Sinopharm Chemical Reagent.Co.,Ltd
Boron	B	C.R,d50:5.71μm	TangShan Weihao Magnesium Powder Co,Ltd
ammonium hydroxide	$NH_3 \cdot H_2O$		Sinopharm Chemical Reagent.Co.,Ltd
ethyl alcohol	CH_3CH_2OH	A.R,purity 99.7%	Sinopharm Chemical Reagent.Co.,Ltd
Magnesium powder	Mg	C.R,d50:45μm	TangShan Weihao Magnesium Powder Co,Ltd
Polytetrafluoroethylene	$(CF_2)n$	C.R,d50:25μm	Sinopharm Chemical Reagent.Co.,Ltd
Phenol formaldehyde	$(C_6H_3OHCH_2)_n$	A.R,purity 99%	Sinopharm Chemical Reagent.Co.,Ltd

Table 1: The raw materials.

with the SEM, so Au should be sprayed onto the B/CuO surface. The crystalline structures of the synthesized product were identified with a powder X-ray diffraction (D8 Advance, Bruker Corp.), employing Cu-Ka radiation (l = 0.15406 nm), with scanning speed 5°/s and angle 2θ in the range 10~80°. The thermal decomposition behavior was investigated using TG-DSC (thermal analyzer SDT-Q600, TA Instrument) over the range from room temperature to 1000°. TG-DSC was carried out with a constant heating

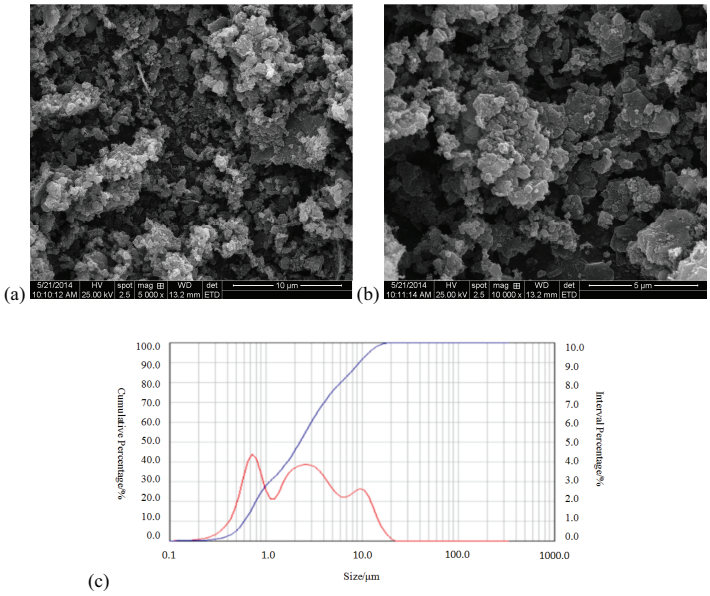

Figure 3: SEM images (a, b) and size distribution (c) of boron particles.

rate. The temperature rose from room temperature to 1000° at a rate of 10°/min. The reaction gas was air, and a constant gas flow of 30 ml/min was adopted for the article. The weight of the sample placed in the aluminum oxide crucible was 3~5 mg. The burning temperature was tested with Infrared Thermometer (IGA 140, Germany IMPAC Instrument Corporation) with measurement range 340~2500°. The probe should aim at the propellant grain and the distance was 2 meters. The temperature of each kind of propellant grain was tested 5 times and the average was recorded as the burning temperature of the propellant .The burning rate was calculated according to the formula μ = de/dt and the mass burning rate was calculated by μm = ρde/dt.

3. Results and Discussion

Figure 3 shows SEM images and size distribution of boron particles. It is representative of the sample particles in size and shape. The boron particles are of submicron and nanometer scale. It can be seen from the SEM images (Fig. 3a, b) that the boron powder is amorphous, and the particles are uneven. The shape of boron is irregular and the powders distribute as reunite state. The boron powder sizes are distributed widely and many peaks are exhibited (Fig. 3c). The average is 0.85 μm 18 μm. The cumulative percentage of the boron powder size from 0.12 μm to 0.85 μm is 22.85%. The percentage of size from 0.85 μm to 5.25 μm is 54.02%. The d10 is 0.61 μm, the d50 is 2.23 μm, and the d90 is 8.97 μm.

The SEM images of the B/CuO nanocomposite thermite used in this study are shown in Figure 4. There are many small crystals surrounding the boron particles and forming the aggregate structure (Fig. 4a). The clear nanometer CuO crystal is shown in Fig. 4b; the compact layer surfaces are laminar and are dispersed with uniform spherical particles. The particles have the same size having average diameter of the microspheres

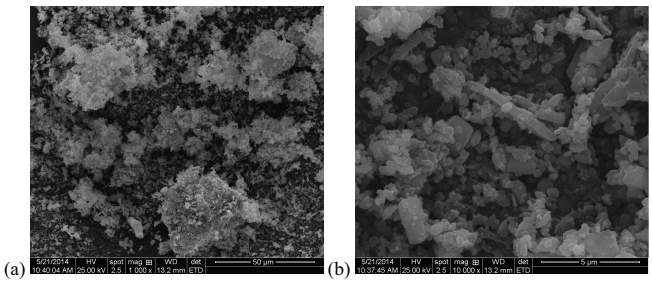

Figure 4: The SEM pictures of B/CuO nanocomposite thermite: (a) microscale, (b) nanoscale.

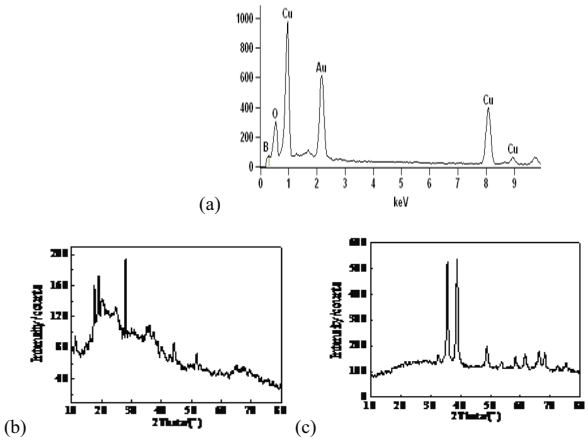

Figure 5: EDS of boron particles (a); XRD patterns of boron particles (b) and B/CuO nanocomposite thermite (c).

50 nm. We could determine that the spherical particles are nano-CuO by means of XRD and EDS.

Figure 5a shows the EDS of boron powder. There are three kinds of chemical elements (B,Mg,Au) signed in the photo. The weight percentage of three elements (B, Mg, Au) is 43.37%, 1.23%, and 55.40% and their atom percentage is 92.36%, 1.17%, and 6.48%, respectively. The sample should be printed with Au dust before testing, so Au element was displayed in the picture. Due to the process of boron powder producing, Mg acted as reducing agent, so there are a few of Mg elements in the powder. However, the boron elements are the main component of the powder. For B/CuO nanocomposite thermite, there are three kinds of elements (B, Cu, O) with percentage 8.39%, 73.12%, and 18.49%, respectively, except for the Au element. The percentage of the three elements is almost the same as that of the raw materials. The peak intensity of boron decreased and that of Mg disappeared after the boron powder was coated by nano-CuO.

It can be seen from the XRD picture of boron particles (Fig. 5b) that the diffraction peaks belong to the elementary substance boron (2θ = 17.5°, 18.8°). In the other positions, the diffraction peaks disappeared or the diffraction strength decreased dramatically and the structure displayed amorphous. The diffraction peak (2θ = 28.0°) belongs to H_3BO_3 or B_2O_3, so the surface of boron particles contains these two compositions. The XRD image of B/CuO nanocomposite thermite (Fig. 5c) shows that the diffraction peaks are consistent with the standard card of CuO, and the nano-CuO belongs to the

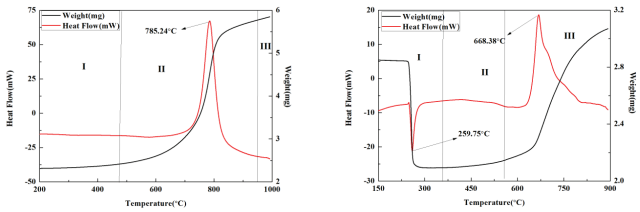

Figure 6: The TG-DSC curve of boron powder (a) and B/CuO nanocomposite thermite.

monoclinic crystal system. There are no other impurity peaks in the picture, so that the nano-CuO is high purity material. There is also not the diffraction peak of boron powder because of the amorphous boron with the low diffraction intensity.

The reaction process of boron with air is shown in Fig. 6a. The TG curve increased slowly from 200° to 478.2°, but the DSC curve was almost flat. It is because there are few boron particles reacting with O_2 and it releases a little heat. When the temperature rises from 478.2° to 600°, the weight of sample is gaining rapidly. The DSC illustrates that the system is in an absorbing heat condition, because there is a thin layer of B_2O_3 melting and the layer may evaporate slightly. In the region of 600° to 850°, the TG curve increases sharply and the weight gains almost two times of the example. The drastic energy releasing process is in this area and the DSC curve has a prominent exothermic peak at 785.24°, which is caused by the significant rate of boron and oxygen reaction. This onset of weight gain is ascribed to the melting of layer of boron oxide; after that O_2 starts to diffuse across the layer and reacts with boron particle as the temperature reaches the melting point of boron oxide. With the temperature increasing to 850°-1000°, the TG curve still rises slowly. This is attributed to the formation of boron oxide on the surface of elemental boron particles that slows down the further diffusion of O_2 across the reaction interface.

At the first stage (150° to 363.2°), the TG curve shows a sharp decline at about 244.36° to 288.09° and there is a narrow endothermic peak in this area. The reason is that there are some $Cu(Ac)_2$ decomposed under this conditions; the products react with O_2 and release heat, so the endothermic peak is sharp-pointed. At the second stage, the weight of nanocomposite thermite increased slowly from 363.2° to 565.3° and mainly of the DSC curve remained unchanged. Because there are a small amount of reactions between the boron powder and nano-CuO, but the reacting heat is transmitted to the inner boron atoms to activate the following reactions. At the third stage (565.3° to 900°), the DSC curve has a high exothermic peak at 668.38° and the TG curve shows a rapid rate of weight gain with increasing temperature. This is due to nano-CuO reacting with boron creating Cu and elemental Cu being oxidized. The result shows that boron powder can react with oxygen at 785.24°C violently, but the B/CuO nanocomposite thermite can react at 668.38°C. This suggests that thermochemistry behavior of boron powder is improved by coating it with nano-CuO and the reaction temperature decreases by about 116.86°C.

Table 2 shows the burning performances of propellants (101.325 Kpa, 25°C); the data is averaged for 3 samples in every group. The line burning rate of B-Mg/PTFE is 4.74

Sample	Average Line Burning Rate /mm·s^{-1}	Average Mass Burning Rate/g·cm^{-2}·s^{-1}	Average Burning Temperature /℃
B-Mg/PTFE	4.74	0.89	1444.39
B/CuO-Mg/PTFE	5.35	1.01	1500.69

Table 2: The burning performances of the sample.

mm/s and that of B/CuO-Mg/PTFE is 5.35 mm/s. The burning rate increased for 12.87%, when the CuO/B nanocomposite thermite was added into the basic formula compared with only boron powder. The mass burning rate of B/CuO-Mg/PTFE is higher than that of control group and the increasing rate is about 13.48%. The burning temperature increased to 56.3° at the same time. The increasing burning rate led to increase of releasing energy per second, so the burning temperature increased. Thus, the heat is fed back to the surface of combustion flame, and the process speeds up the burning rate. All the phenomena show a virtuous circulation.

4. Conclusion

We prepared B/CuO nanocomposite thermite through chemistry precipitation method and revealed the thermochemistry characteristics and the effect of B/CuO on the burning characteristics of Mg-PTFE propellant compared with boron powders. The SEM images showed the B/CuO thermite was in nanometer scale and the XRD and EDS results indicated that the boron particles were coated by nano-CuO layer closely. The TG-DSC curves displayed that the thermochemistry behavior of boron powder was improved by coating it with nano-CuO and the reaction temperature decreased by about 116.86°C compared with boron particles. The burning characteristics of Mg-PTFE propellant with addition of B/CuO thermite were the 12.87% increased rate, 13.48% increased mass burning rate, and 56.3°C increased combustion temperature compared with Mg-PTFE propellant with addition of boron powders. Further research in the field will include improving the boron combustion rate, the ignition performance of boron particles, and the activation energy and pressure exponent of propellant. These studies will be the subjects of subsequent reports.

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