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Preparation and characterization of n-Al/FeF_3 nanothermite

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ABSTRACT

A new type of nanothermite composed of n-Al (metal fuel) and FeF_3 (oxidizer) was investigated in this paper. The thermal behavior and combustion properties of the n-Al/FeF_3 nanothermite were compared with that of n-Al/Fe_2O_3 nanothermite by TG/DSC-MS, XRD, SEM and high-speed camera. The results showed that the decomposition of FeF_3 begins at 300 °C and releases free F ions. The F ions react with Al_2O_3 shell covered on the surface of aluminum. The start and exothermic peak temperatures of the major reaction of n-Al/FeF_3 are at 415 °C and 520 °C respectively, which are 95 °C and 34 °C lower than those of n-Al/Fe_2O_3. Furthermore, the FeF_3 will be reduced to Fe completely at 700 °C. However, the Fe_2O_3 could only be converted to Fe_3O_4. It demonstrates that the reaction of n-Al/FeF_3 is completely, but only a part of n-Al/Fe_2O_3 reacts at 700 °C. The n-Al/FeF_3 has larger, brighter flame and shorter burning time than n-Al/Fe_2O_3 in open air.

1. Introduction

Recently, the thermite plays a more important role in energetic material due to its high energy density [1]. Nanothermite contains metal and metal oxide mixed on nanometer scale, which has been demonstrated to yield up to 1000 times increase in the propagation rate compared to its microsize counterparts [2–4]. In the common nanothermite, aluminum reacts with metal oxide mainly produce Al_2O_3 (boiling point > 3000 °C), the generated Al_2O_3 will form a dense oxide layer which covers the surface of Al. The thermite reaction temperature is usually around 3000 °C [5], so this Al_2O_3 shell will prevent Al contact with oxide and reduce the reaction rate. At the same time, a dense oxide shell of Al_2O_3 is generated in the process of production and storage which influences the ignition performance of nanothermite. However the main reaction product of Al and fluoride is AlF_3 (boiling point = 1291 °C) which is easily heated by reaction heat and escapes from the particle surface. Meanwhile, fluoride will react with the oxide layer of Al. In a word, fluoride plays a very important role in improving the combustion and ignition properties of thermites.

Fluorinated polymer and organic fluoride such as PTFE [6], PVDF [7,8], PFPE [9] and perfluorocarboxylic acid [10] were investigated as a suitable replacement for the traditional metallic oxide in thermites. However, high cost and complex synthesis restrain their application. The application of inorganic fluoride was rarely reported. In 2008, Ernst Christian Koch et.al [11,12] prepared Mg/XeF_2 composition as a new high energy density material. This type of thermites has higher combustion temperature and faster burning rate compared with Mg/PTFE/Viton (MTV). However, XeF_2 is expensive, unstable and easy to hydrolysis. In addition, XeF_2/Mg composition has the risk of spontaneous combustion and explosion in the process of operation. So, using XeF_2 instead of traditional metal oxide is impractical. Traditional metal fluoride, such as NiF_2, CoF_2 and FeF_3, have the higher fluorine content and density compared with organic fluoride. Among them, FeF_3 is widely used as high capacity electrode materials due to its electrochemical reaction properties [13–17]. Fluorine element still has great electronegativity which makes it easy to accept electrons from active metals (Mg, Al, etc.).

In this paper, we presented the metal fluoride (FeF_3) as a substitute for the traditional metal oxide. The objective of this work is to prepare n-Al/FeF_3 nanothermite and study its thermal behavior and combustion properties.

2. Experimental section

2.1. Materials

Nanoaluminum (n-Al, 50 nm, the active aluminum content at about 65% measured by TG method, ALEX, Nanjing Emperor Nano Material Co., Ltd,). Aluminium oxide (n-Al_2O_3, 20 nm, ALEX, Nanjing Emperor Nano Material Co., Ltd,). Iron fluoride (FeF_3, 3 μm, 97%, light green powder, ρ = 3.87 g/cm^3, slightly soluble in water, melting point about 1000 °C, Alfa Aesar). Iron oxide (n-Fe_2O_3, 30 nm, 99.8%, Aladdin Reagents Co., Ltd), n-hexane (99.8%, Sinopharm Chemical Reagent Co.,Ltd).

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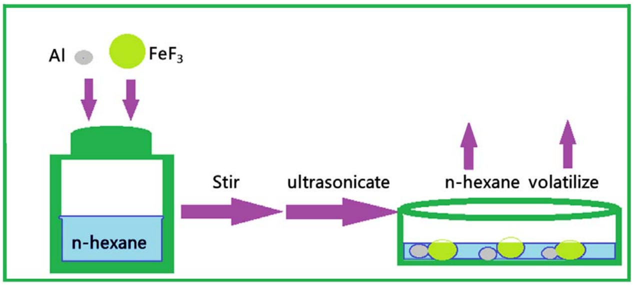

Fig. 1. Schematic diagram of the process.

Table 1
Different composition and proportion of the samples.

No.	Samples	n-Al (wt%)	FeF_3 (wt%)	n-Fe_2O_3 (wt%)
1	n-Al/FeF_3	27	73	/
2	n-Al/Fe_2O_3	34	/	66

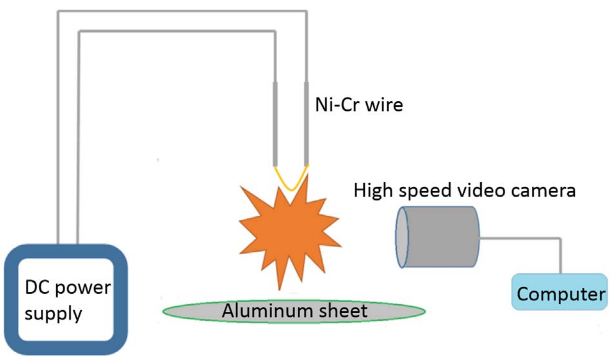

Fig. 2. Combustion test setup.

2.2. Preparation

Ultrasonic mixing method is one of the most simple and effective method to prepare nanothermite [18–22]. As shown in Fig. 1, the samples were prepared by this method. First, 50 mg n-Al and 136 mg FeF_3 (In order to remove the adsorbed water and a small amount of crystal water, FeF_3 was put into muffle with 400 °C and argon shielding before use) were added into 5 mL hexane and stirred 15 min (IKAKMO$_2$ basic Magnetic stirring pump, America). Secondly, the mixture was ultrasonicated 60 min by ultrasonic unit (BRANSON 5510, America) to allow nanoparticle dispersion. Thirdly, the mixture was stirred vigorously for 24 h at room temperature. Finally, the suspension was stoved in 60 °C vacuum oven (DZF6050, Shanghai, Jinghong) for 30 min to completely volatilize the hexane.

Table 1 shows different compositions of samples. Sample 1 and 2 corresponded to a balanced stoichiometry after calculating the effective content of Al and FeF_3 or Fe_2O_3:

$$Al + FeF_3 = AlF_3 + Fe \quad (1)$$

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe \quad (2)$$

(The active aluminum content is about 65%).

3. Characterization

3.1. SEM test

Scanning electron microscopy (SEM, Hitachi, S-4800 II FESEM) was used to characterize the morphology of the n-Al/FeF_3 nanothermite.

3.2. Thermal analysis method

The thermal reactive behavior of the nanothermite was characterized by DSC, TG, MS and XRD. Besides, DSC, TG and MS tests were conducted simultaneously in a NETZSCH STA449C TG/DSC coupled to a NETZSCHQMS403C mass spectrometer from NETZSCH, Germany. 2.5 mg of samples were loaded into an 85 μL Al_2O_3 crucible inside the apparatus and heated from 75 to 700 °C at a typical heating rate of 10 °C min^{-1} under high purity argon (20 mL min^{-1}). A turbo pump was used to evacuate the system to a vacuum of $\sim 1.0 \times 10^{-4}$ mbar. Once the vacuum was finished, the TG/DSC chamber was backfilled with high purity argon to atmospheric pressure. The TG/DSC chamber was connected with the MS by a heated microcapillary (~200 °C), enabling transport of the thermally decomposed species to the MS detector.

The thermal analysis was stopped under different temperature (peak temperature of major peaks) to collect the post-heating residues of the samples. And the residues were characterized by X-ray diffraction (BrukerD8 ADVANCE) to determine the material composition of the sample under different temperatures during the decomposition process.

3.3. Combustion test

The combustion properties of the nanothermite were characterized by homemade combustion test setup. As shown in Fig. 2, an accurately weighed 10 mg sample was placed inside a small aluminum sheet. All samples were ignited at one end by resistively heating a Ni-Cr wire which triggered by an external DC power supply with current of 400 mA and time of 50 ms. A high speed video camera (MotionXtra N3, REDLAKE) was deployed to record the combustion process.

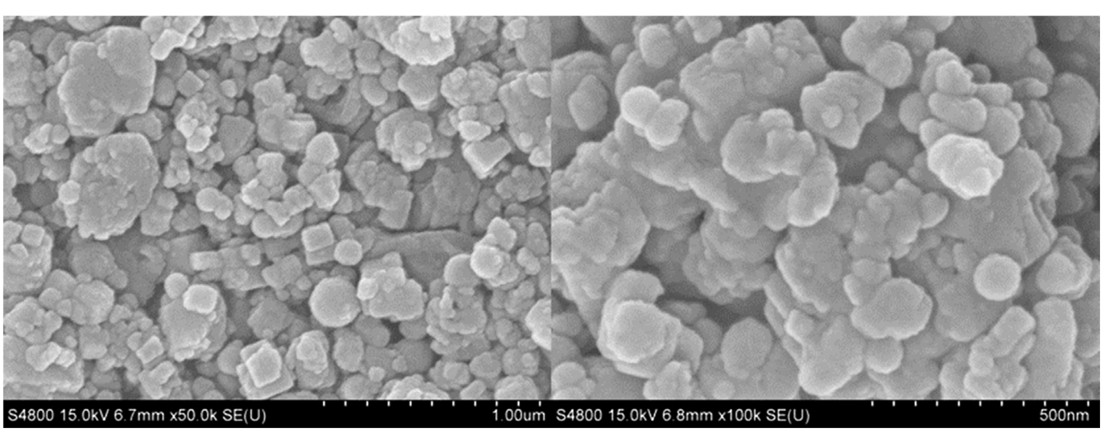

Fig. 3. SEM images of n-Al/FeF_3 nanothermite.