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Metal catalyzed preparation of carbon nanomaterials by hydrogen–oxygen detonation method

Tiejun Zhao[a], Xiaojie Li[a,b], Honghao Yan[a,*]

[a] Department of Engineering Mechanics, Dalian University of Technology, No. 2 Linggong Road, Ganjingzi District, Dalian 116024, Liaoning Province, PR China

[b] State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian 116024, PR China

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ABSTRACT

A hydrogen–oxygen gas detonation was direct initiated by using a 20 J electronic spark, and the pressure and temperature of which were measured by a pressure sensor and high-speed camera, respectively. The results showed the mixed gas was direct initiated in the propagation of detonation wave. The carbon nanomaterials were prepared by decomposition of ferrocene and cobalt (III) acetylacetonate ($Co(acac)_3$), a the samples were characterized by X-ray diffractometer, transmission electron microscope, engergy dispersive X-ray detector and Raman spectrometer. The results indicated that carbon-encapsulated metal nanoparticles were fabricated by using ferrocene, ferrocene–$Co(acac)_3$ as a precursor, and the core–shell nanostructures were carbon-encapsulated Fe/Fe_3C nanoparticles (Fe@C) and carbon-encapsulated Co nanoparticles (Co@C). However, the Fe–Co alloy was absent in sample from ferrocene–$Co(acac)_3$. It is interesting that the sample from $Co(acac)_3$ were Co@C and multi-walled carbon nanotubes (MWCNTs), and the crystallization degrees of the carbon and Co nanoparticles in the MWCNTs were higher than that of in carbon-encapsulated metal nanoparticles, however, the degree of graphitization of the powders was low. The physical properties of precursors, hydrogen content and rapid reaction were the main factors which contributed to the different morphologies and the absence of Fe–Co alloy.

1. Introduction

Carbon encapsulated metal nanoparticles (M@C) and carbon nanotubes (CNTs) are very important carbon nanomaterials, which have special and unique physical and chemical properties [1,2]. As we know, nanoscale metal particles are so unstable that they can be oxidized easily because of the nanoscale effect. Therefore, in order to prevent the nanoscale metal particles from oxidation and make full use of the properties of metal, researchers take advantage of the high stability of carbon to generate a core–shell structure [3] and tube structure [4]. Especially, the carbon nanomaterials, which contain magnetic metal nanoparticles (such as Fe, Co, Ni etc.), are widely applied in electromagnetic field for data storage and wave absorption, medical field for medicine carrier, environment purification for oil sorption, and so on [5–8]. So far, the preparation of carbon nanomaterials is not stopped. The chemical vapor deposition (CVD) method is the most acceptable way to prepare M@C and CNTs [9,10], which can generate different morphologies by control the gas ratio and dosage of catalyst. The arc-discharge method is another method to fabricate M@C and CNTs [11], which can be supported by plasma to control the morphology [12,13]. Some researchers have studied a relative easy operation and effective way to prepare M@C, such as flame and combustion method [14]. Iron and nickel are used as the catalyst to growth M@C and CNTs in flame method [15,16]. In recent years, our group has studied the preparation of carbon nanomaterials by detonation method [17–21], which demonstrates that detonation method is an easy, high efficiency and feasible way to prepare carbon nanomaterials. Specially, the samples from the gaseous detonation method is much safer and higher purity than explosive detonation which attracts much attention [22]. Preparing nanomaterials via a continuous gaseous detonation prcess is the goal for industrial preparation of nanomaterial. It is possible to prepare nanomaterials via continuous detonation method based on the theory of detonation–deflagration, and our group explored the feasibility of continuous detonation in 2011 [23]. However, it needs further research to solve the problems of precursor addition and powders collection.

In the gaseous detonation method, the energy comes from the detonation (deflagration) of a combustible mixture gas with oxygen. Thus, the initiation energy of the combustible gas and the wave propagation mode in a tube are the key points to which many scholars paid much attention because of the security of

* Corresponding author.
E-mail address: yanhh@dlut.edu.cn (H. Yan).

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industrial production and fuel engine [24,25]. The direct initiation model proposes that the combustible gas could propagate as a detonation wave without deflagration to detonation transition (DDT) process [26,27]. Lee proposed a model that the critical direction initiation energy is related to cell size, which has been proved by experiments and numerical simulation [27]. Zhang et al. [28,29] studied the critical energy by experiments in detail. High-speed photography technique can be used to record the trajectory of wave front, which is used to calculate the wave velocity and estimate the wave propagation mode.

Though many achievements have been accomplished both gaseous detonation preparing nanomaterials and gaseous detonation theory [30,31], it is uncertain the mode of initiation and propagation of the hydrogen–oxygen. In the present study, a pressure sensor and the high-speed camera were used to measure the pressure and the trajectory of the wave in a homemade tube and determine the propagation of combustion wave. The phase and morphologies of the samples were also studied by using different precursors with $2H_2$–O_2 gaseous detonation.

2. Theory and experiment

2.1. Theory

Electronic spark is one of the most important direct initiation methods. Lee proposed a surface energy model [26], which indicated that the surface area of the minimum detonation kernel evolved from a planar should equal to the surface area of critical tube.

$$\pi (d_{cr}/2)^2 = 4\pi R_s^{*2} \tag{1}$$

where d_{cr} is the critical diameter of tube; R_s^* represents the detonation kernel size. According to the strong blast wave theory, the initiation energy was given as

$$E_{cr} = 4\pi I\gamma p_0 M_{CJ}^2 R_s^{*3} \tag{2}$$

where E_{cr} represents the critical initiation energy; I is a numerical constant; γ is specific heat ratio; p_0 is the initial pressure; M_{CJ} represents the mach number at CJ plane. Therefore, the relationship of critical initiation energy and critical diameter can be obtained via Eqs. (1) and (2), as expressed in equation below.

$$E_{cr} = \frac{1}{16}\pi I\gamma p_0 M_{CJ}^2 d_c^3 \tag{3}$$

The empirical correlation of the critical diameter of tube is $d_{cr} = 13\lambda$, where λ is the cell size, then it can obtain:

$$E_{cr} = \frac{2197}{16}\pi I\rho_0 D_{CJ}^2 \lambda^3 \tag{4}$$

where ρ_0 is the initial density of the mixed gas; D_{CJ} is the velocity at CJ plane; I is a numerical constant.

It is clear from Eq. (4) that the critical initiation energy is in proportional to cell size. It reports that the cell size is affected greatly by initial pressure, equivalence ratio and proportion of diluent [32]. The cell size of $2H_2$–O_2 is about 1 mm under 1 atm, thus, the critical diameter of tube is about 13 mm ($d_{cr} = 13\lambda$). The detonation tube used in present experiments is 95.0 mm in inner diameter and 1100.0 mm in length. The value of diameter is much larger than 13 mm, therefore, the detonation wave could propagate stably, and the cell size would not be changed much under the same condition. Zhang et al. [28,29], Kamenskihs et al. [33], and Liu et al. [24] have studied the critical energy for direct initiation through experiments or numerical simulation in detail, including high initial pressure, proportion of diluent and equivalence ratio. The results demonstrate that the direct initiation energy of $2H_2$–O_2 at 1 atm is less than 10 J. Therefore, in present experiments, a 20 J ignition energy electric spark was used to detonate the mixture gas of $2H_2$–O_2.

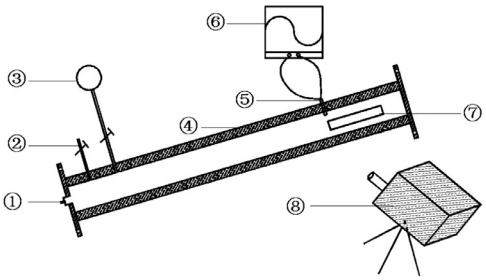

Fig. 1. Diagram of gaseous detonation tube and high-speed camera, (① spark, ② gaseous injecting and vacuuming hole, ③ vacuum gauge, ④ heating system, ⑤ pressure sensor, ⑥ pressure recorder, ⑦ visible window and ⑧ high-speed camera).

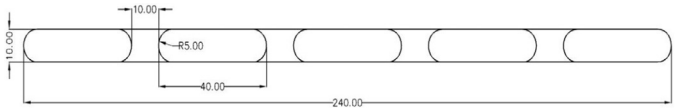

Fig. 2. Diagram of the visible window (unit: mm).

2.2. Experiment

The carbon nanostructures were fabricated in a home-made gaseous detonation tube. The tube is designed with 95.0 mm in inner diameter and 1100.0 mm in length, which satisfies with the propagation of detonation wave criterion. The ignition energy of electric spark is 20 J to make sure the mixture gas is direct detonation. In order to verify the detonation wave propagation, a high-speed camera (Fastcam ultime APX photron made in Japan) was used as shown in Fig. 1. The camera could make 40,000 frames per second and the camera lens points at the visible window to observe the detonation propagation. The parameters of the visible window are shown in Fig. 2, which is 240.00 mm in length with 5 high temperature resistance glass windows. The glass window is 24.00 mm long and has two semicircles with 5.00 mm in radius at the both ends. The distance of each window is 10.00 mm. The gaseous detonation propagation was studied by using hydrogen and oxygen with 2:1 in molar ratio.

Ferrocene, an useful metal organic matter, is usually used to prepare carbon nanotubes [34] and carbon encapsulated iron nanoparticles [35]. It is reported that the sublimation temperature of ferrocene is about 100 °C [36] and the decomposition temperature is as low as 350 °C [37]. In present study, the Fe–C nanostructure was prepared by using ferrocene as metal catalyst and carbon resource, hydrogen and oxygen mixture gas as energy. The ferrocene powders, the mass of which is 2 g, were placed uniformly in the tube, then vacuumed the tube and heated to 120 °C and made ferrocene sublimation. The hydrogen and oxygen were filled with molar ratio of 2:1. About 10 min later, the gas mixture was ignited by a 20 J electro spark. The black powders were collected and marked as Fe–C after 5 min.

The boiling point of cobalt (III) acetylacetonate ($Co(acac)_3$) is about 150 °C at ordinary pressure, and $Co(acac)_3$ would decompose at 125–150 °C [38] and evaporate at 190 °C [39]. In the preparation of Co-nanostructure experiment, the operation process was similar with preparing of Fe–C nanostructure except for the initial temperature of 160 °C. $Co(acac)_3$ was used as the precursor, which was decomposed by the detonation of hydrogen and oxygen in a molar ratio of 2:1. The dosage of ($Co(acac)_3$) was 2 g and the black product was collected and marked as Co–C.

In order to research the possibility of preparing Fe–Co alloy carbon nanostructure, 3 g of ferrocene and 1 g of $Co(acac)_3$ were mixed and place in the tube. After vacuuming, heating and gases