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ARTICLE

Synthesis of Carbon-Encapsulated Iron Nanoparticles by Gaseous Detonation of Hydrogen and Oxygen at Different Temperatures within Detonation Tube

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Abstract: Using ferrocene as precursor, the mixed gas of hydrogen and oxygen as the source of explosion, the carbon encapsulated iron nanoparticles were prepared in a detonation tube. The influences of initial reactive temperature and heat treatment on the products of particles were studied. The characteristics of detonation products were tested by X-ray diffraction (XRD), transmission electron microscope (TEM), and vibrating sample magnetometer (VSM). Results show that the carbon encapsulated nanoparticles exhibit the shapes of sphere or spheroid. With reaction temperature increasing, the grain sizes of carbon encapsulated iron nanoparticles are 30~50 nm and tend to be uniform, which indicates that the initial reaction temperature directly affects the grain sizes of the generated particles. Through the analysis of magnetic hysteresis loops of detonation products, the saturated magnetization (M_s) decreases as the temperature of heat treatment increases, and the hysteresis loops are in a relatively "thin" shape, but still have higher coercivity, indicating that the synthesized carbon-encapsulated iron nanomaterials present the dual natures of the hard magnetic and the paramagnetic.

Key words: gaseous detonation; ferrocene; hydrogen and oxygen gas; detonation tube

Carbon-encapsulated metal nanoparticles (referred to as CEMNPs), also known as carbon-encapsulated nano metallic grain, are a new type of nano carbon/metal composites, which are of several layers of graphite films tightly around the metal nanoparticles with ordered arrangement, and the nano metal particles are at the core location, forming a core-shell structure. Since the nano metal particles are coated with carbon and isolated to air, it then solves the issue of nano metal particles not being able to exist stably in the air. For the enormously potential value in chemical, materials, physics and other fields, many experts have done a lot of research of the materials[1-10]. CEMNPs also have unique electrical[11,12], magnetic[13] and optical[14] natures, therefore, they find wide applications in functional magnetic materials, microelectronics, biomedical, redox catalysis, optical radiation technology and other fields.

In the present paper, the gaseous detonation synthesis method was adopted. It is simple, rapid and economical, and the alloy composition can be easily adjusted, as well as possess other advantages. Gaseous detonation method is quite similar to explosives detonation, which uses the energy generated from the detonation of mixed gas. In the gaseous detonation method, explosive mixture gas consisting of combustible gases (hydrogen, acetylene, methane, etc.) and oxygen, as well as nitrate or chloride salts with low boiling point is ignited in the detonation tube with electrical sparks to synthesize nano-oxides.

1 Experiment

In the gaseous detonation synthesis of carbon-encapsulated nano iron by ferrocene [$(C_5H_5)_2Fe$], main elements participating the reactions are C, H, O, Fe. It is assumed *a*, *b*, *c* and *d*, denoting the atomic molar amount of carbon, hydrogen,

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oxygen and iron, respectively, in the precursor and gas mixture used in gaseous detonation. According to the chemical reaction formula, the following reaction will occur:

$$C_aH_bO_cFe_d \rightarrow a\,CO_2 + \frac{b}{2}H_2O + \frac{d}{3}Fe_3O_4 \tag{1}$$

Then, oxygen balance (OB) can be determined according to the B-W rules:

$$OB = \frac{[d-(2a+\frac{b}{2}+\frac{3d}{4})]}{M}\times 16 \tag{2}$$

Where, a, b and d are the molar mass of the carbon, hydrogen and iron, respectively; M is the molar mass of the precursor, kg/mol.

In order to synthesize carbon encapsulated iron nanoparticles successfully, all elements within the system that can participate in the reaction must achieve negative oxygen balance, i.e., OB<0.

Since the pressure value for gaseous detonation is no more than 10 MPa, the gas can be assumed as ideal gas; thus the ideal gas law could be used, which is known as the Clapeyron Equation[15], and the volume of gas charged into the tube can be determined through the principle of partial pressure, as follows:

$$PV = nRT \tag{3}$$

where, P, V, n, R and T represent pressure, volume, molar amount, gas coefficient (constant) and temperature, respectively.

It is assumed that R, T and V are invariants, and then the relationship between P and V is linear, i.e.,

$$P_1 : P_2 : P_3 \ldots = V_1 : V_2 : V_3 \ldots = n_1 : n_2 : n_3 \ldots \tag{4}$$

The purpose of this experiment is to observe the effect of temperature changes of the detonation tube on the composition. 1# and 2# denote the experiments in which ferrocene was not sublimated, while 3# and 4# are experiments after the sublimation of ferrocene. Table 1 lists the initial state condition for the experiments. According to the calculation, if 3.5 g ferrocene was completely sublimated into gas, that is, the comparison between the volume of ferrocene (0.4 L) and the volume of detonation tube (7.8 L) was negligible, then the choice for volume ratio of hydrogen to oxygen being 2:1 was done. The molar constitution of each element under each working condition is shown in Table 2.

Table 1 Initial experimental conditions at different temperatures

No.	T/K	P/MPa	Ferrocene/g	n(H):n(O)
1#	293	0.1	3.5	2:1
2#	353	0.1	3.5	2:1
3#	393	0.1	3.5	2:1
4#	423	0.1	3.5	2:1

Table 2 Molar composition and oxygen balance of each element in the precursor

Experiment No.	Element composition				n(H):n(O)	OB
	H	O	C	Fe		
1#~4#	0.652	0.232	0.188	0.0188	2.8:1	<0

2 Results and Discussion

2.1 XRD analysis

Fig.1 is XRD patterns of synthesized carbon- encapsulated nanoparticles at different temperatures within the detonation tube. It can be seen that four XRD patterns all have a "bulge" at around 2θ=26.40°, which means that the product contains element carbon. Diffraction peaks appear near 44.64°, 65.08° and 82.34°, corresponding to the XRD peaks of element iron. In the reaction products, once iron exists in elemental form, we can initially determine the presence of carbon-encapsulated iron nanoparticles. In addition, other diffraction peaks mainly are Fe_3C. The formation of Fe_3C is mainly due to conditions of high temperature and pressure generated during the detonation of hydrogen and oxygen.

2.2 Topography analysis

TEM can visually reflect the topographies of the product. TEM image of each working condition is shown in Fig.2.

From the figures, it can be seen that larger particles exist in all of the four working conditions, and the particles show as oval shape. As the temperature rises, the grain size tends to be uniform; we can see that the sizes of generated particles are directly affected by the initial reaction temperature. The reason is that as the temperature rises, ferrocene sublimates from solid to gaseous powder, and grain uniform shape particles appear.

It can be seen form Table 3 that whether it is after or before sublimation, the average grain sizes of iron produced from ferrocene, are in the range of 30 nm to 50 nm.

2.3 Magnetic property analysis

JDW-13 Vibrating Sample Magnetometer (test temperature: 298 K, maximum magnetic: 675.57 kA/m) was adopted to carry out heat treatment of the material and analyze the hysteresis loop. Fig.3 is the hysteresis loop of the synthesized materials after heat treatment, and Table 4 gives relative data corresponding to the hysteresis loops. It can be found that the saturated magnetization (M_s) decreases as the heat treatment temperature rises, decreasing from 84.7 $A\cdot m^2/kg$ to 71.93

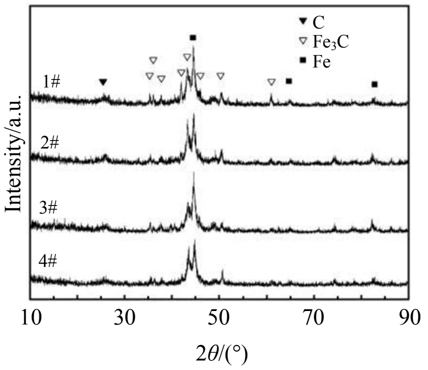

Fig.1 XRD patterns of CEMNPs at different temperatures