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ARTICLE

Fabrication of Carbon Encapsulated ZrC Nanoparticles by Electrical Explosion of Zr Wire in Ethanol

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Abstract: The method of electrical explosion of metal wire in organic liquid was adopted to prepare carbon encapsulated nanoparticles. In the medium of absolute ethyl alcohol, under the high-voltage pulse current (HVPC), the high purity zirconium wire became fusion, gasification, expansion and explosion, accompanied with separating of carbon out of ethanol and reaction of carbon and zirconium, and carbon encapsulated ZrC nanoparticles formed. The energy, voltage and current in the experiments were measured to analyze the influence of them on the products. The products were analyzed by X-ray diffraction technique (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The results show that the carbon encapsulated ZrC nanoparticles are fabricated successfully. The diameter range is between 10~150 nm. For the voltage of 4, 8 and 12 kV, the average size of the products is 24.9, 41.4 and 43.9 nm, respectively. Finally, the procedure and mechanism of fabrication of the carbon encapsulated ZrC nanoparticles were discussed preliminarily.

Key words: electrical explosion; carbon encapsulated nano-particles; zirconium carbide; formation mechanism

Carbon-coated nanoparticles are a kind of metal particles or metal compound nanoparticles encapsulated by carbon shell, and the shell is amorphous carbon or fullerene. The shell and core are connected by physical or chemical force[1]. This material was originally detected by Ruoff[2] and Tomita[3], when they used graphite rode as an anode to prepare carbon nano-tube by an arc-discharge method, and carbon-coated metal nanoparticles was found in the products. This carbon coating materials not only have a protection from outside influence or corrosion[4], but also can prevent agglomeration of nanoparticles. Carbon-coated nano-materials have broad application prospects in the field of energy, magnetic storage, chemical catalysis and bio-medical. Generally, carbon-coated nanomaterials can be fabricated by different methods such as arc discharge[5], pyrolysis[6], CVD[7] etc.

In this paper, a new approach, electrical explosion of metal (selected as zirconium) wire in medium of absolute ethyl alcohol, was attempted to fabricate the carbon-coated nanoparticles. The products were analyzed by XRD, TEM and HRTEM methods, and the formation mechanism as well as the particles size of the products were also discussed.

1 Experiment

Electrical explosion is a new method to prepare carbon-coated nanoparticles. High-voltage pulse current was imput in the metal wire transiently and make the wire explosion (as shown in Fig.1). In the medium of organic liquid, the wire was fused and vaporized by the high-density current until being heated to explode, the sputtered liquid metal would be cooled quickly and grow into metal nanoparticles. The carbon separated out from alcohol reacted with metal and coated it.

The zirconium wire with the purity 99%, length 50 mm, diameter 0.14 mm was selected and fixed between the electrodes and submerged 3 cm below the surface of the absolute ethyl alcohol. The high-voltage electricity was charged to the capacitors which was set as 10 μF. To analyze

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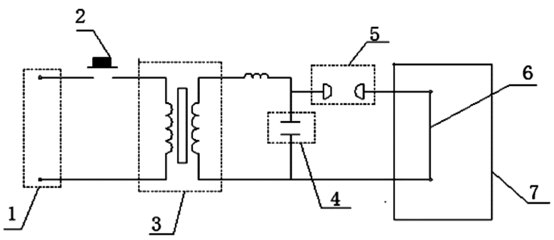

1-Charging circuit; 2-Charging switch; 3-High-voltage generator; 4-Capacitor; 5-Discharge switch; 6-Metal wire; 7-Reaction container

Fig.1 Circuit diagram of electrical explosion

Table 1 Preparation parameters of ZrC nanoparticles

Material	Purity/%	Diameter/mm	Length/mm	Capacity/μf	Voltage/kV
Zr wire	99	0.14	50	10	4
	99	0.14	50	10	8
	99	0.14	50	10	12

the influence of the voltage on the products, three different voltage of capacitors 4, 8 and 12 kV were considered in the experiments (Table 1). After the explosion of zirconium wire in the absolute ethyl alcohol, the product was collected by the liquid core filters and stored in the absolute ethyl alcohol.

2 Electrical Explosion Analysis

The current, voltage and energy curves of electrical explosion in absolute ethanol are shown in Fig.2a (the current and voltage curves were measured and the energy curve was calculated by the current and voltage). The electrical explosion process of metal wire can be divided into five stages[8]. (1) The heating stage of the wire (t_1–t_2). At this stage, the voltage and the current rise steadily, and the deposition rate increases until the equilibrium point t_2. (2) Melting stage of the wire (t_2–t_3). At this stage, the resistance decreases accompanied with the dropping voltage and rising current. The energy deposition almost remains unchanged until the gasification point t_3. (3) The vaporization stage of the wire (t_3–t_4). At this stage, the gaseous metal results in the quick increasing of the resistance, the current decreases and the voltage rises to the maximum, and the energy deposition will rise quickly. (4) Explosion stage of the wire (t_4). At this stage, the gaseous metal and ethyl alcohol inflate rapidly and explode, and some of the carbon separate out from alcohol. (5) The arc through stage (after t_4). The powder in the medium continues to discharge, and breakdown the medium between the electrode and forms the electric arc. Part of the carbon separated out from alcohol reacts with zirconium core and ZrC nanoparticles form, and then some other carbon coats the ZrC nanoparticles steadily.

Fig.2b, 2c and 2d show the current, voltage and energy curves of zirconium wire when the charged voltage of the capacitor is 4, 8 and 12 kV. From Fig.2, it can be found that with the increasing of the voltage, the time of the electrical explosion decreases, and the current, voltage and energy deposition changes significantly, which reflects a more drastic explosion.

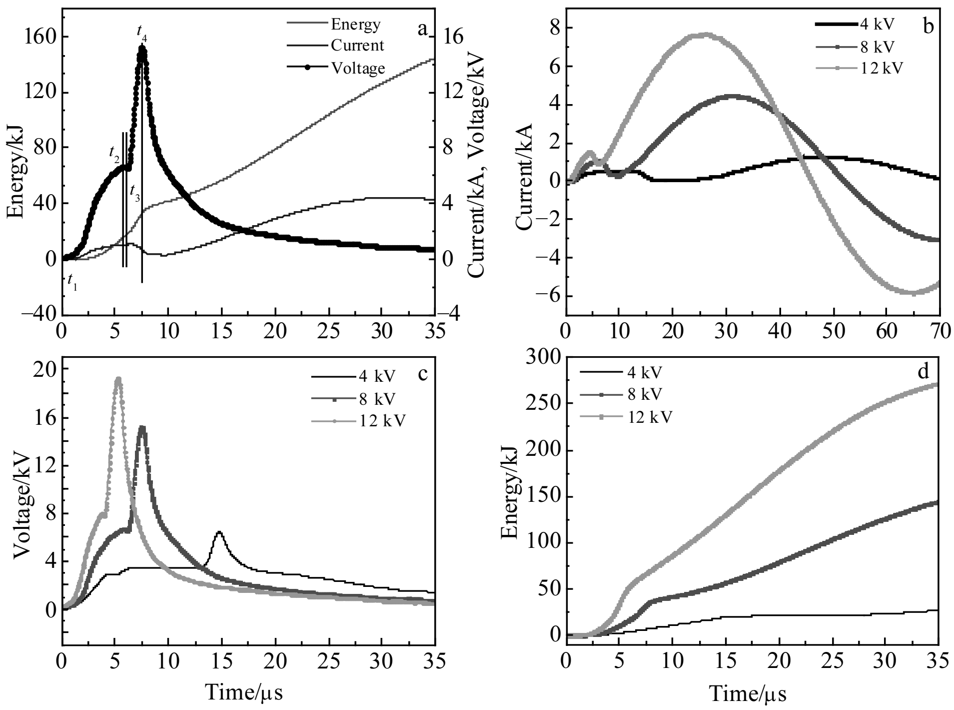

Fig.2 Current, voltage and energy curves (a) of zirconium wire electrical explosion in the absolute ethanol under charged voltage of 8 kV; the current (b), voltage (c) and energy (d) curves of zirconium wire electrical explosion under charged voltage of 4, 8, 12 kV

3 Characterization of the Products

3.1 XRD analysis

There exist five distinct diffraction peaks in Fig.3. The angles 2θ corresponding to the diffraction peaks are 33.1°, 38.4°, 55.5°, 66.1°, 69.5° and the crystal faces correspond to (111), (200), (220), (311), (222). They are corresponded with ZrC of cubic phase standard. Except traces of ZrO_2 peaks, there is no obvious peak miscellaneous. Because there is no diffraction peaks of C apparently, the coating of the core is amorphous carbon. ZrC is a typical structure like NaCl type face-centered cubic. As the standard of XRD pattern, the three kinds of nanomaterial offset to low angle. During the explosion, the lack of C atom from the frame will cause lattice vacancies, and H, O atoms will slip into the frame and fill up from crystal lattice. This will result in the unbalance of C and Zr atoms as the skewing of the peak shows.

The XRD analysis shows that for the explosion of zirconium wire with length 50 mm and diameter 0.14 mm at the charged voltage 4 kV, the average size of the carbon encapsulated ZrC nanoparticles is 24.9 nm. For the zirconium wire with length of 50 mm, diameter of 0.14 mm, exploded at the electrical explosion of 8 kV voltage, the average size of the carbon encapsulated ZrC nanoparticles is 41.1 nm. For the zirconium wire with length of 50 mm, diameter of 0.14 mm, exploded at the electrical explosion of 12 kV voltage, the average size of the carbon encapsulated ZrC nanoparticles is 43.9 nm.

3.2 TEM analysis

TEM was adopted to analyze the morphology, particle size, and tissue distribution of the carbon-coated nanoparticles.

Fig.4a is TEM image of the carbon encapsulated ZrC nanoparticles fabricated at 8 kV voltage. It can be found that the particles are spherical or ellipsoidal. Particles size analysis shows that the size distribution is between 30~130 nm and disperse well. Fig.4b, 4c and 4d are the HRTEM images of products from zirconium wire exploded under 4, 8 and 12 kV voltage, respectively. Those pictures show that the thickness of the carbon layer is about 2~5 nm. The onion-like structure of the particles shows that the carbon shell is assembled layer by layer toform a multilayer coating.

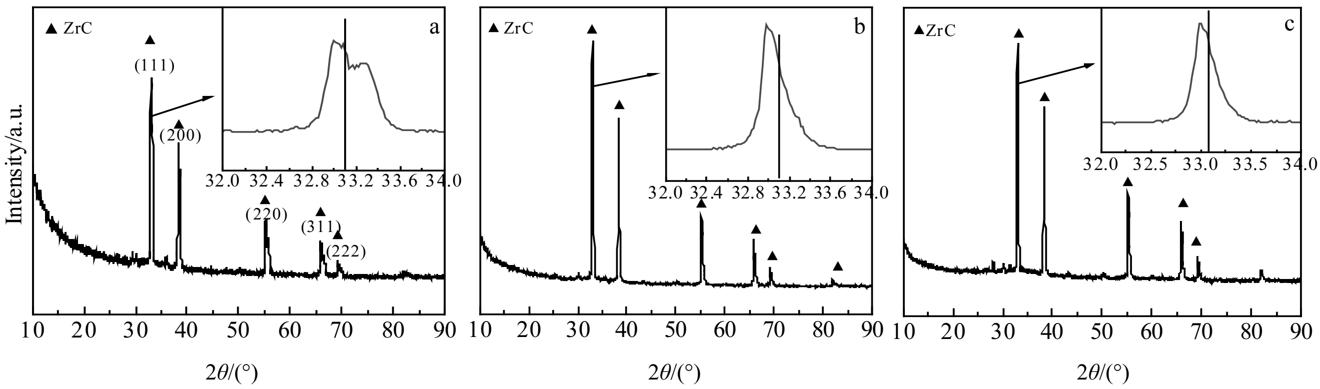

Fig.3 XRD patterns of products fabricated under 4 kV (a), 8 kV (b) and 12 kV (c) voltage

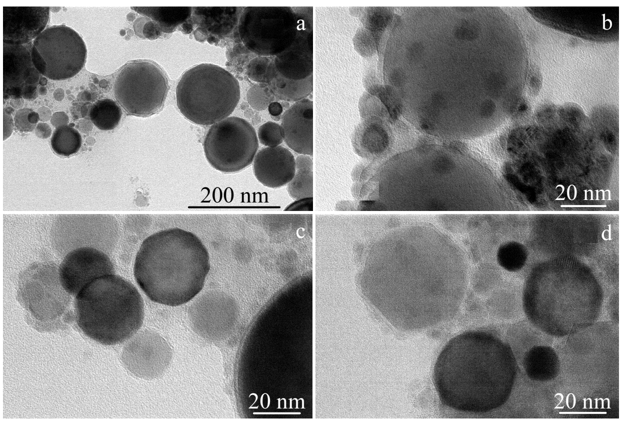

Fig.4 TEM image of products fabricated under 8 kV voltage (a) and HRTEM images of products fabricated under 4 kV (b), 8 kV (c) and 12 kV (d) voltage

4 Formation Mechanism of Carbon Encapsulated ZrC Nanoparticles

Under the specific conditions, ethanol can provide the carbon source for the preparation of carbon coated nanomaterials. Electrical explosion is a new method to prepare carbon-coated nanoparticles, and carbon atoms diffuse into the mixing vapor and saturated to separate. A portion of carbon react with Zr to form ZrC nanoparticles. Others grow to amorphous carbon and will be adsorbed to the surface of the ZrC nanoparticles, and form the carbon-coated layer. These walls of carbon are not structure of graphitic layers, but amorphous carbon[9].

The separation of carbon can be described by the equation as follows:

$$CH_3CH_2OH+O_2 \xrightarrow{\text{high pressure and temperature}} 2C+3H_2O \quad (1)$$

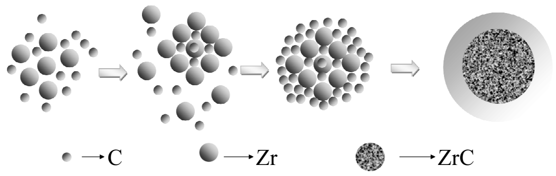

Fig.5 Formation mechanism of carbon encapsulated ZrC nanoparticles

$$Zr+C \xrightarrow{\text{high pressure and temperature}} ZrC \quad (2)$$

The formation procedure of the carbon encapsulated ZrC nanoparticles is shown as follows: (1) Under the high temperature and high pressure, carbon and zirconium evaporated from the evaporator source impact each other and form a small group of atoms. They continue to attract the atoms around. (2) These atomic group impact and combine with the atoms from the vapour, which is an iterative process. When the number of atoms reaches the critical value, the atomic group will further combine with gas atoms and grow toward to a stable radical. (3) The stable radical impact with redundant carbon, the supersaturation carbon deposit to the surface of radical and form to stable carbon atoms surrounded by nucleation. (4) The surface carbon atoms move and diffuse continually to form the stable carbon-coated nanoparticles.

5 Conclusions

1) Carbon encapsulated ZrC nanoparticles can be prepared by electrical explosion of the zirconium wire in the medium of absolute ethyl alcohol. This method has the advantages such as voltage energy concentration, high controllability and stable response.

2) Carbon encapsulated ZrC nanoparticles prepared by the electrical explosion method have the intact core-shell structures. They are spherical or ellipsoidal, and their diameter size ranges between 10~150 nm. For the voltage of 4, 8 and 12 kV, the average size of the products is 24.9, 41.4 and 43.9 nm, respectively.

3) The formation procedure of the carbon encapsulated ZrC nanoparticles can be explained as follows: (1) The separation of carbon out of ethanol under high pressure and high temperature and formation of zirconium nano-particle during explosion of zirconium wire. (2) Carbon and zirconium impact each other and react to form ZrC nano-particles. (3) The supersaturation carbon deposit to the surface of ZrC nano-particles to form stable carbon atoms surrounded by nucleation. (4) The surface carbon atom movs and diffuses continually to form the stable carbon-coated ZrC nano-particles.

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乙醇中锆丝电爆炸法制备碳包覆 ZrC 纳米颗粒

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摘 要：采用在有机液体中进行金属丝电爆炸的方法制备了碳包覆纳米颗粒。以无水乙醇为介质，对高纯度锆丝施加高压脉冲电流，锆丝在高密度电流下迅速熔化、气化、膨胀并爆炸，伴随着高温、高压下乙醇中碳的析出和碳与锆反应及包覆过程，制备出碳包覆 ZrC 纳米粉体颗粒。对电爆炸过程中的能量、电流、电压对产物的影响进行了分析，通过 XRD、TEM、HRTEM 等分析了产物特征。结果表明：产物为球状碳包覆碳化锆纳米颗粒，粒径分布在 10~150 nm 之间；在 4、8、12 kV 电压下，产物平均粒径分别为 24.9、41.1、43.9 nm。最后，对碳包覆 ZrC 纳米颗粒的形成机理进行了初步的探讨。

关键词：电爆炸；碳包覆纳米颗粒；碳化锆；形成机制

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