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ARTICLE

Synthesis of Zirconium Dioxide Nanoparticles by Electrical Explosion of Zirconium Wire and Characteristics

Wang Jinxiang[1], Peng Chucai[1,2], Dai Hehua[3], Lu Fujia[1], Zhao Zheng[4]

[1] National Key Laboratory of Transient Physics, Nanjing University of Science and Technology, Nanjing 210094, China; [2] College of Civil Engineering & Architecture, Hunan Institute of Science and Technology, Yueyang 414006, China; [3] Nanjing Baotai Special Materials Co., Ltd., Nanjing 211100,China; [4] School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

Abstract: Zirconium dioxide (ZrO_2) nanoparticles were synthesized by electrical explosion of zirconium wire in the air. The process of wire explosion and particles formation were analyzed according to the measured current, voltage and calculated deposited energy waveforms. Results show that electrical breakdown through the vapor of zirconium wire and the surrounding air result in an explosion and stop the energy deposition in wire. By scanning electron microscopy (SEM) and transmission electron microscope (TEM), it is found that the morphologies of synthesized nanoparticles are nearly spherical and the diameters range from 30.6 to 69.4 nanometers. X-ray diffraction (XRD) analysis show that the powders consist of monoclinic ZrO_2 (*m*- ZrO_2) and tetragonal ZrO_2 (*t*- ZrO_2). The content of *t*-ZrO_2 increases while the content of *m*-ZrO_2 decreases with the increasing charging voltage. In addition the average sizes of the *m*-ZrO_2 and *t*-ZrO_2 both increase when the charging voltage increases.

Key words: zirconium dioxide nanoparticles; electrical explosion; energy deposition; electrical breakdown

Zirconium dioxide is important ceramic with a variety of excellent properties such as high melting point, high resistivity, high refractive index, low thermal expansion coefficient, etc. [1,2]. So it can be used to enhance the electrochemical stability of lithium ion battery[3], to manufacture high-quality semiconductor and to improve the strength of hydroxyapatite bone cement[4, 5]. It is meaningful to find a high-quality and efficient preparation method for the broad application prospects and development potential of nanosized zirconium dioxide.

Electrical explosion of wire (EEW) is a new technique for the preparation of nano-materials. It uses a strong pulse current to heat the wire to vaporization and even to plasma state, and then the explosion products condense into nanoparticles in a certain medium (such as inert gas, water, etc.)[6, 7]. Some researches have been done on the dependences of the particle properties and productivity upon the explosion conditions to optimize their selection in a device [8-11]. However, most of the research work were focused on the stage after explosion. The process before explosion and the influence of deposited energy on particle properties were rarely discussed.

In this paper, Zirconium dioxide (ZrO_2) nanoparticles were prepared by electrical explosion of zirconium wire in the air and the characteristics of the products were analyzed. Also, the whole process of Zirconium wire explosion and the influence of charging energy of storage capacitor on particles properties were discussed in detail.

1 Experiment

The schematic diagram of the experimental setup used for fabrication of nano ZrO_2 powders by wire explosion is shown in Fig.1. It includes two parts: charging circuit and discharging circuit. After closing the charging switch, the capacitor bank would be charged from the high voltage DC power supply. Pulsed large current from the capacitors would be applied to the zirconium wire after the gap switch was closed. Powders were collected by a membrane filter (Nylon Membrane Filters, 0.1 μm) and stored in the alcohol.

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Corresponding author: Wang Jinxiang, Ph. D., Professor, Nanjing University of Science and Technology, Nanjing 210094, P. R. China, Tel: 0086-25-84315276, E-mail: wjx@njust.edu.cn

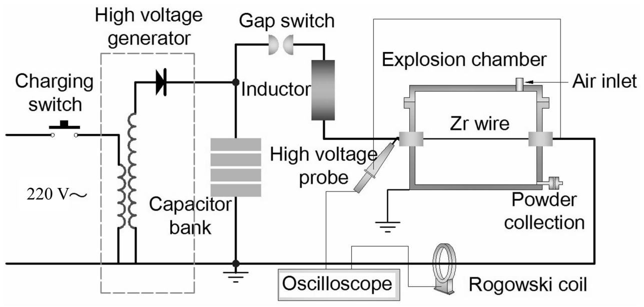

Fig.1 Schematic diagram of the experimental setup

In the experiments, the pure Zirconium wires (more than 99.9%) with the diameter of 0.14 mm were adopted. Single zirconium wire was placed between the two electrodes (the span length: 50 mm) in the chamber. The capacitor bank of 10 μF was charged up to 3, 4, 5 and 6 kV. The total circuit inductance L was 14.6 μH. The typical voltage between the electrodes $u(t)$ and the current of the electrical discharge circuit $i(t)$ were measured by the voltage probe (Tektronix P6015A) and a Rogowski coil (BL4.745.3411), respectively.

2 Results and Discussion

Fig.2 shows the discharge voltage, current and deposited energy waveforms of a zirconium wire when the capacitor bank is charged up to 4 kV. It shows the typical features of wires explosion. The voltage suddenly increases and subsequently falls rapidly after a peak value[12]. The voltage increase is attributed to the increase in resistivity of the wire due to vaporization. An arc discharge, which is generated by electrical breakdown through the vapor of zirconium wire and the surrounding air at the time of point α, leads to a voltage drop and a current increase at the same time. The explosion took place just at this time due to the sharp drop of magnetic pressure and the loss of thermodynamic stability of a superheated liquid in wire [13]. The magnetic pressure P at point r along the radius of the conductor and the central magnetic pressure P_c are given by,

$$P = P_c(1-\frac{r^2}{a^2}) \quad (1)$$

$$P_c = \frac{\mu_0 i_w(t)^2}{4\pi^2 a^2} \quad (2)$$

Where μ_0 is the vacuum permittivity, a is the radius of the wire and $i_w(t)$ is the current flow through the wire [11]. Obviously, the formation of arc discharge will significantly reduce $i_w(t)$ and P_c. Then the thermal pressure will drive the superheated liquid and vapor to expand outward.

Fig.3 shows the voltage, current and deposited energy waveforms of wire explosion for the charging voltage of 3, 4, 5 and 6 kV. It can be found that the rising rate of voltage and current increased with the increase of charging voltage. E_e is the deposited energy in the zirconium wire up to the time of

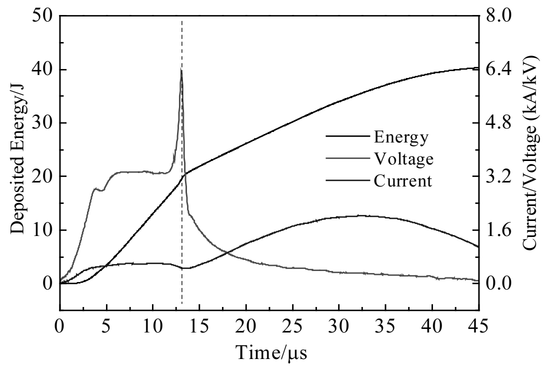

Fig.2 Typical voltage, current and deposited energy waveforms of the Zr wire during explosion

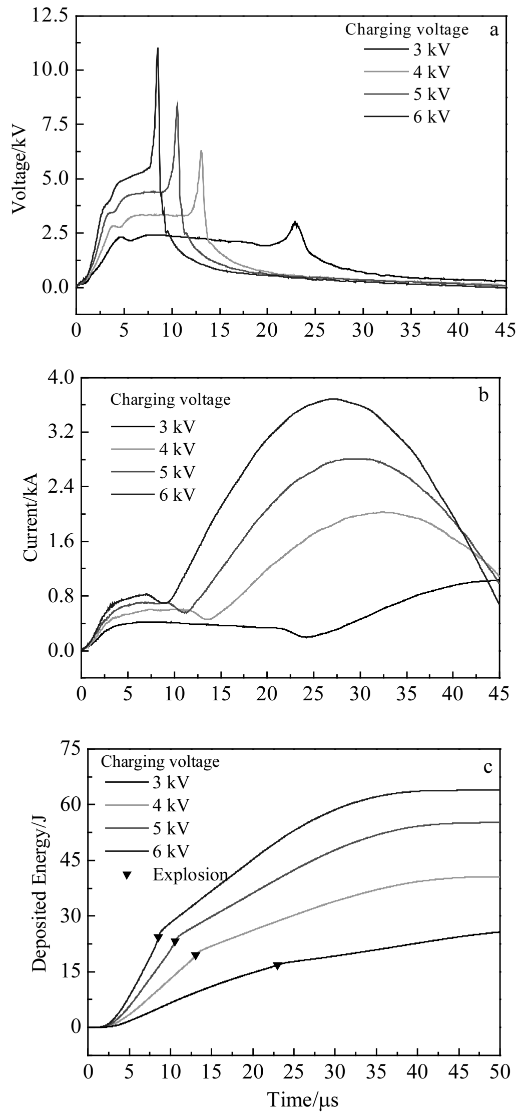

Fig.3 Voltage (a), current (b) and deposited energy (c) for wire explosion under the charging voltage of 3, 4, 5 and 6 kV

the initial explosion t_e, which can be calculated by Eqs. (3)~(5):

$$u_r(t) = u(t) - L_w \frac{di}{dt} - i(t)\frac{dL_w}{dt} \quad (3)$$

$$L_w = \frac{\mu_0 l}{2\pi}\left(\ln\frac{2l}{a} - 0.75\right) \quad (4)$$

$$E_e = \int_0^{t_e} u_r(t)\cdot i(t)dt \quad (5)$$

$$E_s = \pi a^2 l \rho e_s \quad (6)$$

Where, $u_r(t)$, L_w and l are the resistance voltage, inductance and effective length of the wire, respectively. The calculated E_e is 16.8, 19.46, 23.22 and 24.32 J for the charging voltage of 3, 4, 5 and 6 kV, respectively, which are all lower than the sublimation energy E_s=32.92 J, which are calculated by Eqs.(6):

Where, the specific sublimation energy e_s and density ρ of zirconium is 6.58 kJ/g and 6.5 g/cm^3, respectively. It can be found that E_e increases with the energy supplied. However, it is difficult to evaporate completely for the wire at the beginning of explosion due to the disruptive discharge, even if the capacitor energy storage is several times higher than E_s. Therefore, there should be an extreme deposited energy for every specific experimental condition. After the explosion, the zirconium dioxide nanoparticles form rapidly with the thermalizing collisions and chemical reaction between metal particles and surrounding oxygen.

Typical scanning electron microscopy (SEM) and transmission electron microscope (TEM) images of nanopowders obtained by explosion of a zirconium wire are given in Fig.4a and Fig.4b, respectively. Most particles are nearly spherical in shape and the diameters range from 1 nm to 100 nm. It is deduced that the particles with 1~10 nm in diameter are formed by condensation of gaseous phase and most particles of large size are probably from the liquid drops, which are formed during the explosion of zirconium wire.

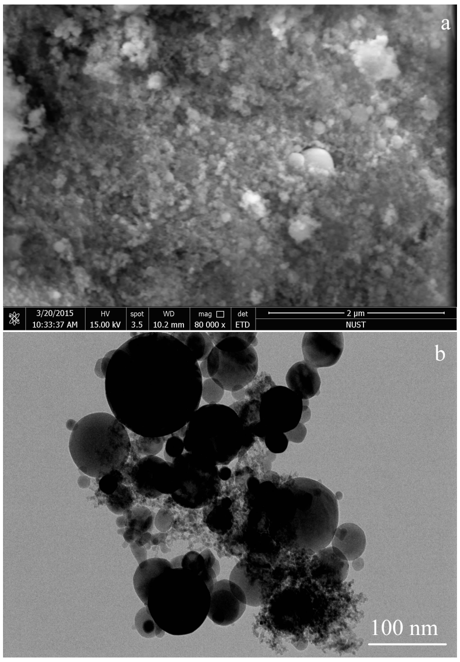

Fig.4 SEM (a) and TEM (b) images for samples obtained by zirconium wire explosion in the air

The X-ray diffraction (XRD) pattern of the powder is shown in Fig.5. It reveals that the powders consist of monoclinic (*m*) and tetragonal (*t*) ZrO_2, matched with JCPDF card 78-1807 and 80-0784, respectively. There are no presence of cubic (*c*) ZrO_2, zirconium nitride and other phases in the patterns of collected nanoparticles. Based on the XRD results, the phase composition and average crystalline size of the synthesized powders are calculated and shown in Table 1. It can be found that the particles are characterized by an increased content (more than 60 wt%) of *t*-ZrO_2, and the fraction of *m*-ZrO_2 decreases with the increased charging voltage. The previous researches show that the shock wave is linearly proportional to the specific energy supplied to the exploding wire [14], which decide the expansion and cooling rate of liquid-vapor mixture. The particles have not enough time to form ordered crystalline structure phase and complete the transition *t-m* due to the high expansion and cooling rate. Therefore, the more energy supplied, the higher content of *t*-ZrO_2 is produced.

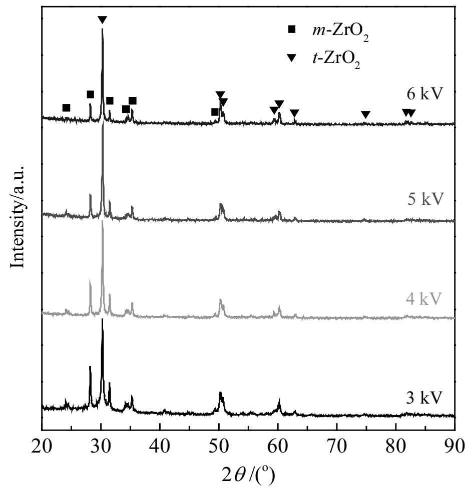

Fig.5 XRD patterns of samples obtained with zirconium wire explosion in the air

Table 1 Phase composition and average crystalline size of explosion products

Charging voltage/kV	Phase composition/wt%		Average size/nm	
	m-ZrO_2	*t*-ZrO_2	*m*-ZrO_2	*t*-ZrO_2
3	38.9	61.1	62.7	30.6
4	32.2	67.8	66.7	35.8
5	26.6	73.4	67.3	36.2
6	21.1	78.9	69.4	43.5

The *m*-ZrO_2 are bigger in average size than *t*-ZrO_2, and both of their sizes are increased with the enhanced charging voltage, which is opposite to some other metals [15, 16]. These characteristics of products can be explained as follows. According to the so-called effect of dimensional stabilization, if the size of its structural elements exceeds the critical size R_{cr} (equal to 30 nm), the *t*-ZrO_2 in nonstabilized zirconia is unstable at room temperature. In the opposite case, *t*-ZrO_2 can become a thermodynamically equilibrium phase at low temperatures and persist at room temperature, which probably accounts for the high content of *t*-ZrO_2 with the diameter of nearly 30 nm [17]. Based on the experimental data shown in Table 1, it is deduced that the critical size R_{cr} increases with the cooling rate, which lead to the increase of average size of both *m*-ZrO_2 and *t*-ZrO_2.

3 Conclusions

1) The method of electrical explosion of zirconium wire in the air is introduced for preparation of zirconium dioxide (ZrO_2) nanoparticles. It is difficult to completely evaporate for the zirconium wire at the beginning of explosion due to the electrical breakdown, even if the capacitor energy storage is several times higher than the sublimation energy of zirconium wire. The powders generated are nearly spherical in shape and the diameters are less than 100 nanometers.

2) The produced zirconium dioxide consists of monoclinic and tetragonal phases. The monoclinic phase has a larger size and more content than tetragonal phase. Under our experimental conditions, the average size of particles and the content ratio of the tetragonal phase to the monoclinic one increase with the increasing charging energy of storage capacitor.

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锆丝电爆炸法制备氧化锆纳米颗粒及其特征

王金相[1]，彭楚才[1,2]，戴和华[3]，卢孚嘉[1]，赵 铮[4]

(1. 南京理工大学 瞬态物理国家重点实验室，江苏 南京 210094)
(2. 湖南理工学院 土木建筑工程学院，湖南 岳阳 414006)
(3. 南京宝泰特种材料股份有限公司，江苏 南京 211100)
(4. 南京理工大学 能源与动力学院，江苏 南京 210094)

摘 要：在空气中采用锆丝点爆炸法合成了纳米二氧化锆颗粒，根据实测电流、电压和由此计算得到的能量沉积波形分析了电爆炸和纳米颗粒形成过程。发现锆丝气化后在锆丝蒸气和空气中形成电击穿现象诱发电爆炸并截断锆丝中的能量沉积。通过扫描电镜和透射电镜对产物进行了分析，发现纳米二氧化锆颗粒形貌呈近球形，粒度分布在 30.6~69.4 nm 之间。X 射线衍射分析表明, 产物由单斜晶型（*m*-ZrO_2）和四方晶型（*t*- ZrO_2）二氧化锆组成，随着充电电压的提高，四方晶型二氧化锆含量增加而单斜晶型含量变小，二者粒度都呈变大趋势。

关键词：氧化锆纳米颗粒; 电爆炸; 能量沉积; 电击穿

作者简介：王金相，男，1978 年生，博士，教授，博士生导师，南京理工大学瞬态物理国家重点实验室，江苏 南京 210094，电话：025-84315276，E-mail: wjx@njust.edu.cn