

Generation and Characterization of Zirconium Carbide Nanoparticles by Wire Explosion Process

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Zirconium carbide nanoparticles were produced by wire explosion process by exploding zirconium conductor in methane ambience. X-ray diffraction studies of the particles produced by wire explosion process confirm the formation of cubic zirconium carbide particles. The results of the study indicates that unreacted zirconium content in the zirconium carbide powder could be reduced by exploding the zirconium conductor by depositing energy of three times the sublimation energy in 100 kPa methane pressure. Selected area electron diffraction (SAED) analysis confirms that particles produced are cubic zirconium carbide particles. Transmission electron microscopy analysis indicates that zirconium carbide nanoparticles are spherical in shape and the particle size distribution follows log-normal distribution with the mean particle size of about 20 nm. [doi:10.2320/matertrans.M2012021]

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1. Introduction

Nanoparticles often have good electrical, thermal, mechanical, chemical, optical and magnetic properties, which could be achieved by engineering the size, shape, morphology and composition of the particles.^{1,2)} Zirconium Carbide (ZrC) is extensively used to produce cutting tools, and as a wear resistant coating material. Also it is a selective material for the fourth generation nuclear plants because of its high melting point, solid-state phase stability, and good thermo-mechanical and thermo-chemical properties.^{3,4)}

Zirconium carbide particles were generated by various processes and the size of the particles produced lies in the range of 50–200 nm.^{5–8)} Recently Jiang and Yatsui⁹⁾ have demonstrated that it is possible to produce nanoparticles by wire explosion process and have demonstrated it to be a simplest and a cost-effective process. In the wire explosion technique, by providing proper energy to the conductor to evaporate and by maintaining suitable medium for carburizing, it is possible to generate carbide nanoparticles along with a precise control over size and shape of the particle.

Having known all this, in the present work a methodical experimental study was carried out to produce zirconium carbide nanoparticles of much lower size, by exploding zirconium conductor in a methane atmosphere. The generated nano powders were characterized by wide angle X-ray diffraction (WAXD) and by selected area electron diffraction (SAED) analysis. The size and shape of the particle formed by wire explosion process were analyzed through transmission electron microscope (TEM) studies. The particle size distribution studies were performed by adopting log-normal probability distribution. The relationship between size of the nanoparticles generated by the wire explosion process and the ambient pressure of the methane were analyzed.

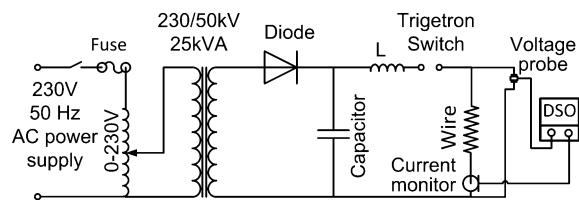


Fig. 1 Experimental setup.

2. Experimental Details

The wire explosion or the electric explosion process is basically an adiabatic process. The process of nanoparticle formation by wire explosion process includes conversion of solid conducting wire to a vapour state by injecting a high magnitude of current (of the order 10^8 A/cm^2) in a micro-second duration. The vaporized metal is allowed to cause local reaction with the surrounding medium instantaneously and cooled to form nucleation of particle and then stabilized to retain its size and shape to form nano sized particles. Thus the wire explosion process is basically a one step process of generating nanoparticles.

Figure 1 shows the basic circuit used for exploding the conducting wires to form nano powders. The switch is a high voltage trigatron-gap, R is resistance of the exploding wire and L is the inductance contributed by internal inductance of the capacitor and lead inductance. The basic circuit works like an under damped RLC circuit and maximum power it could deliver is VI . The capacitor is charged by the rectifier circuit and discharged through the wire through trigatron unit at required time. Energy stored in the capacitor $W = \frac{1}{2} CV^2$ where, C is the capacitance of the capacitor and V is the charging voltage of the capacitor. Typical value of voltage and capacitance are shown in Table 1. By varying the charging voltage, it is possible to deposit the required energy.

Table 1 Experimental details.

Capacitance	Charging voltage	Wire diameter	Length of wire
3 μF	27.5 kV	0.5 mm	39 mm

By closing the switch S , the voltage appears across the wire and the current (controlled by the RLC circuit) rises, causing Joule heating of the conductor.

The magnitude, shape and duration of current flow in the circuit depend on resistance of the exploding conductor (R) and the inductance (L) in the circuit.¹⁰⁾ In present work, circuit parameters match the condition for an under-damped RLC circuit, where

$$\frac{R^2}{4L^2} < \frac{1}{LC}. \quad (1)$$

Then the magnitude of current flow in the circuit can be written as

$$i(t) = \frac{Ve^{-\frac{R}{2L}t}}{\sqrt{\frac{L}{C} - \frac{R^2}{4}}} \sin\left(\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}t\right). \quad (2)$$

Typical voltage across R and the current flow through it were measured at the time of explosion, using voltage probe (EP-50k, PEEC, A Japan) and current probe (Pearson Electronics, USA Current transformer Model No-101), is shown in Fig. 2. Minimum Energy supplied to the conductor for vaporization will be equal to the sublimation energy (W_s) of that conductor. The sublimation/vaporization energy of zirconium is 7.7 kJ/gr. According to the present experimental conditions, the value of W/W_s (the ratio between amount of energy deposited and amount of energy required for vaporization) is varied from 2 to 4.8.

In present study, wide angle X-ray diffraction (WAXD) measurements were performed using Bruker Discover D8 diffractometer with Cu-K α radiation of wavelength 0.15425 nm. The particle size and morphology of the sample and the corresponding selected area electron diffraction (SAED) analysis was carried out by CM12 transmission electron microscope (TEM). Particle sizes were evaluated from TEM bright field images, based on the projected area of each particle's equivalent diameter (Heywood diameter), and used for the analysis of particle size distribution. Number of particles analyzed from each sample was around 500.

3. Results and Discussion

In the wire explosion process, where, the amount of energy to be deposited to the wire conductor has higher influence on the size of nanoparticles formed. A minimum energy to be deposited should be equal to number of moles times the latent heat of vaporization of the metal conductor. The energy required for vaporization of material W_s , in general can be calculated as¹¹⁾

$$W_s = C_s * \Delta T_m + h_v + h_m + C_f * \Delta T \quad (3)$$

where C_s is the heat capacity of the exploding conductor, $\Delta T_m = T_m - T_0$, T_m is the melting temperature, T_0 is the

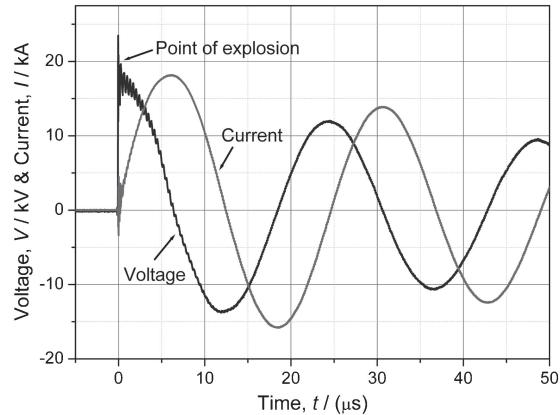


Fig. 2 Typical voltage and current waveforms measured during wire explosion process.

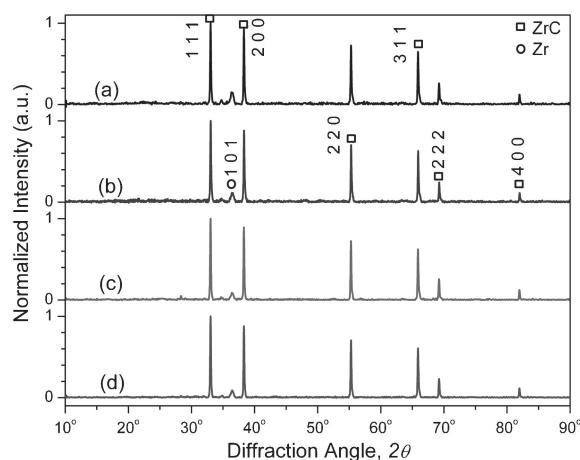


Fig. 3 WAXD pattern of the zirconium carbide nanoparticles produced in methane ambience at different pressures (a) 25 kPa (b) 50 kPa (c) 100 kPa (d) 150 kPa and $W/W_s = 3$.

initial temperature, T is the final temperature, h_m is the latent heat of melting, h_v is the latent heat of vaporization and C_f is the heat capacity of the liquid metal. In the present study, zirconium carbide nanoparticles were generated by exploding zirconium conductor in methane ambience (which acts as a carburizing agent). The vaporized metal reacts with carburizing methane gas in the surrounding medium, which are at room temperature, allowing nucleation of zirconium carbide nanoparticles. The zirconium carbide particles produced by wire explosion process was dark black in color.

Figure 3 shows WAXD pattern of the zirconium carbide nanoparticles obtained by exploding zirconium conductor in methane atmosphere, at different pressures. The WAXD pattern of the powder produced by wire explosion process, reflect cubic phase zirconium carbide characteristic diffraction peaks of 2θ at 33.04, 38.3, 55.3, 65.9, 69.3 and at 82.05.¹²⁾ In general, based on the WAXD results it could be concluded that the particle produced by exploding zirconium conductor in methane ambience produces zirconium carbide particles.

The peak at 36.5 is the characteristic peak of unreacted hexagonal zirconium. It is also observed that, no sub carbide peaks were found. Operating pressure of methane gas during wire explosion process, have certain influence on the particle

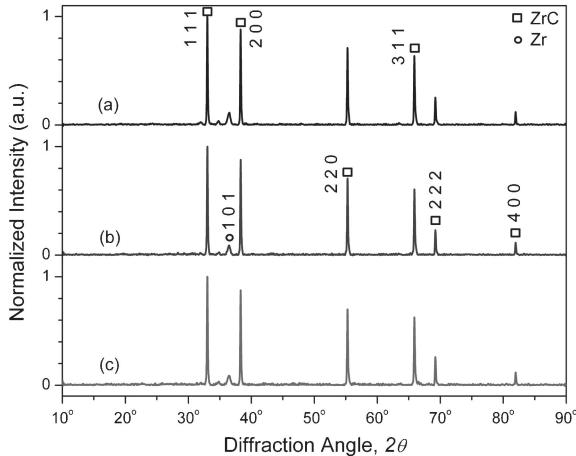


Fig. 4 WAXD pattern of the zirconium carbide nanoparticles produced in methane ambience for different level of energy (a) $W/W_s = 2$ (b) $W/W_s = 3$ (c) $W/W_s = 4.8$ (methane pressure 150 kPa).

produced. At lower pressure unreacted zirconium particle peaks are observed. When the pressure is increased, the magnitude of unreacted zirconium is reduced. When the pressure of the methane gas ambience is increased above 100 kPa, no characteristic variation in reduction of unreacted zirconium observed. The analysis of the study also indicates no traces of zirconium oxide in the powder generated by the wire explosion process.

Figure 4 shows WAXD pattern of the zirconium carbide nanoparticles obtained by exploding zirconium conductor by depositing different levels of energy, in methane 150 kPa atmosphere. It is noticed that increase in methane pressure has drastically reduced the unreacted zirconium content in the zirconium carbide powder produced. It is also observed that increase in energy deposition to the exploding conductor has also further reduced the unreacted zirconium phase. In general it could be concluded that by maintaining operating pressure at 100 kPa and by depositing energy of $W/W_s = 3$, it is possible to obtain zirconium carbide with minimum level of unreacted zirconium. In general, during wire explosion process, the local temperature causes pyrolysis of gaseous methane leading to the formation of free carbon. This free carbon reacts with nucleated zirconium nanoparticles and forms zirconium carbide. When the local pressure is increased, the concentration of methane is increased thereby increasing number of carbon atoms present near the wire explosion zone, enhancing the formation of zirconium carbide. Also, when the zirconium nanoparticle nucleates, its surface area become high and increase in carbon atoms in the medium allows reaction to form ZrC. Similarly, when the energy deposited to the exploding conductor is increased, the local temperature rise would be high and will sustain the local temperature for longer time, thus allowing the nucleated particles sufficiently longer time to form zirconium carbide particle, which results in reduced amount of unreacted zirconium. The crystallite size of the formed zirconium carbide nanoparticles is calculated using Debye Scherer equation. It is observed that, irrespective of operating pressure of the methane ambience and the amount of energy deposited, the crystallite size of the particle is 9 nm.

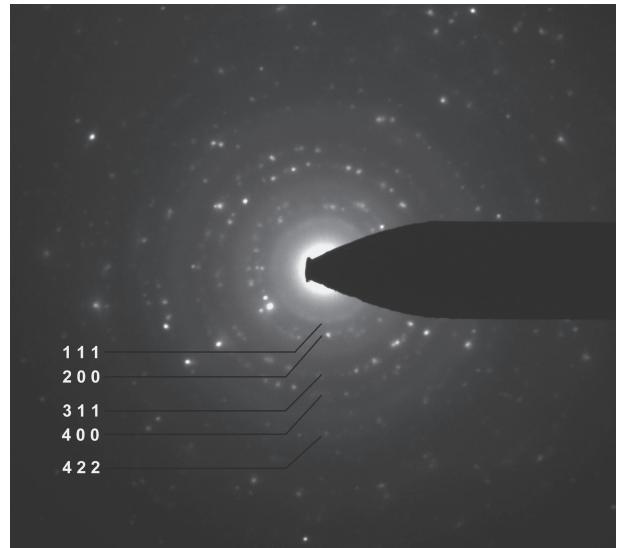


Fig. 5 Typical SAED pattern of Zirconium carbide nanoparticles.

Figure 5 shows typical SAED pattern obtained for the zirconium carbide particle confirming that the produced particle by wire explosion process is Cubic structured Zirconium carbide. Figures 6(a) and 6(b) show typical TEM pictures of zirconium carbide nanoparticles obtained by exploding zirconium conductor in methane ambience (at different pressures) and by depositing different level of energy deposition respectively. The synthesized zirconium carbide nanoparticles are spherical in shape. The particle size lies in the range of a few nm up to 100 nm approximately. It is observed that the particle size measurement follows the log-normal distribution.¹³⁾

Where,

$$f(d) = \frac{1}{\sqrt{2\pi}d \log \sigma_g} \exp\left(\left\{-\frac{(\log d - \log D_{50})^2}{2(\log \sigma_g)^2}\right\}\right) \quad (4)$$

$$\log \sigma_g = \sqrt{\frac{\sum n_i (\log d_i - \log D_{50})^2}{\sum n_i}} \quad (5)$$

$$\log D_{50} = \frac{\sum n_i \log d_i}{\sum n_i}. \quad (6)$$

Here $f(d)$ denotes the log-normal distribution, d is the particle diameter, n_i is the number of particles with diameter d_i , D_{50} is the median diameter, and σ_g is the geometrical standard deviation.

Figures 7(a) and 7(b) show the particle size distribution of the produced zirconium carbide nanoparticles by wire explosion process in methane ambience (at different pressures) and by depositing different levels of energy respectively. The mean size of the particles calculated through distribution studies is shown in Table 2. It is observed that increase in operating pressure shows increase in size of the particle. It is also observed that, irrespective of operating pressure, increase in applied energy shows a marginal reduction in size of the particle. In general, a minimum size of about 20 nm zirconium carbide particles could be produced by wire explosion process.

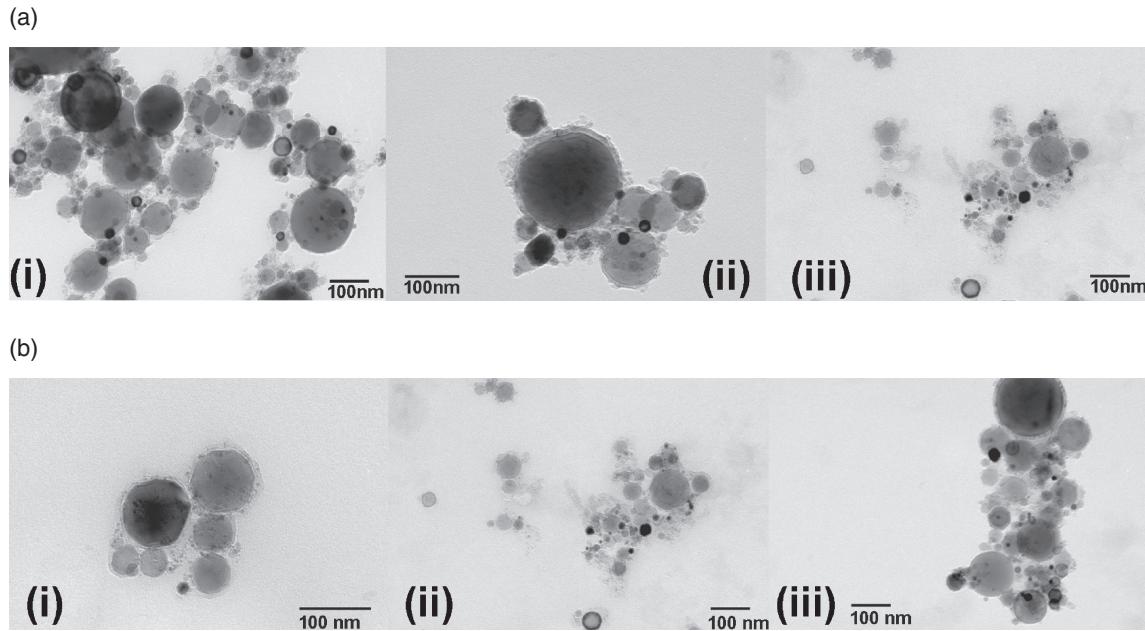


Fig. 6 TEM pictures of zirconium carbide nanoparticles produced by wire explosion process. (a) ZrC nanoparticles for $W/W_s = 3$ in methane ambience (i) 50 kPa (ii) 100 kPa (iii) 150 kPa (b) ZrC nanoparticles produced due to different level of energy deposition with methane ambience at 150 kPa pressure (i) $W/W_s = 2$ (ii) $W/W_s = 3$ (iii) $W/W_s = 4.8$.

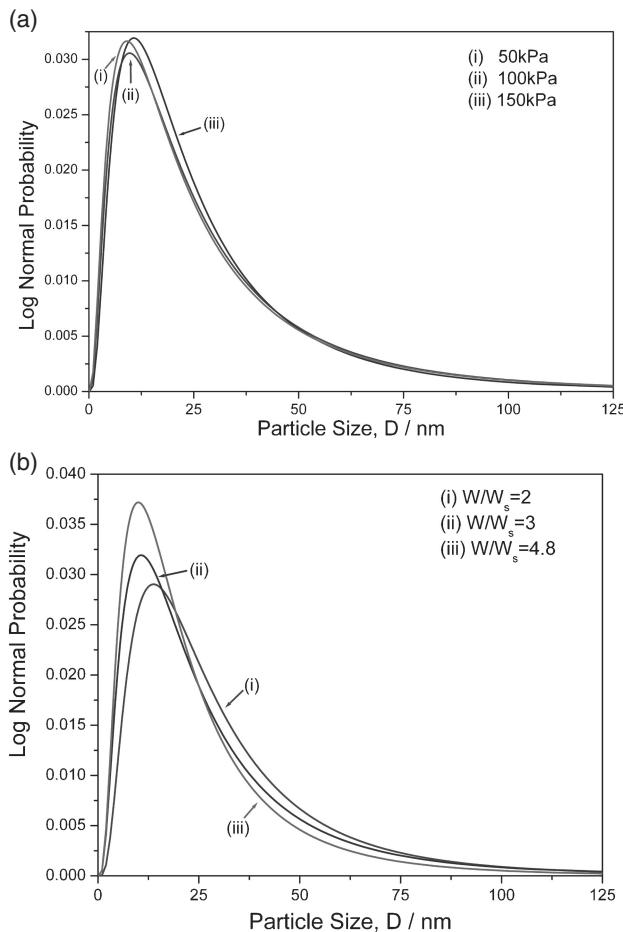


Fig. 7 Particle size distribution of the produced zirconium carbide nanoparticles. (a) In methane ambience for different pressures ($W/W_s = 3$) (b) different level of energy deposition (methane pressure 150 kPa).

Table 2 Variation in mean diameter and geometric standard deviation of the Zirconium carbide particles.

(a) Produced for $W/W_s = 3$ in methane ambient at various pressures

Pressure (kPa)	Geometric mean (D_{50} , nm)	Geometric standard deviation
50	20.93	2.50
100	21.75	2.46
150	21.25	2.29

(b) Produced for various W/W_s ratios in methane ambient at 150 kPa pressure

W/W_s ratio	Geometric mean (D_{50} , nm)	Geometric standard deviation
2	24.25	2.12
3	21.25	2.29
4.8	18.58	2.20

4. Conclusions

The zirconium carbide nanoparticles were produced by wire explosion process by exploding zirconium conductor in methane ambience. WAXD studies confirm the formation of cubic phase zirconium carbide particle. No traces of zirconium oxide were found in the WAXD pattern of the zirconium carbide powders produced. Unreacted zirconium content in zirconium carbide particle produced by wire explosion process could be reduced by depositing energy $W/W_s = 3$ and with methane ambience pressure at 100 kPa. It is observed that crystallite size of the particle produced by wire explosion process is 9 nm. Selected area electron diffraction analysis confirms that particles produced are of cubic zirconium carbide particle. TEM analysis indicates that

zirconium carbide particles are spherical in shape and its size varies in the range of few nm to 100 nm, following log-normal distribution. The mean size of the zirconium carbide particles produced by wire explosion process is about 20 nm.

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REFERENCES

- 1) H. Gleiter: *Acta Mater.* **48** (2000) 1–29.
- 2) C. P. Poole, Jr. and F. J. Owens: *Introduction to Nanotechnology*, (John Wiley & Sons, Inc. Hoboken, New Jersey, 2003).
- 3) X. M. He, L. Shu, H. B. Li and D. Weng: *J. Mater. Res.* **14** (1999) 615–618.
- 4) G. H. Reynolds, J. C. Janvier, J. L. Kaae and J. P. Morlevat: *J. Nucl. Mater.* **62** (1976) 9–16.
- 5) M. D. Sacks, C. Wang, Z. Yang and A. Jain: *J. Mater. Sci.* **39** (2004) 6057–6066.
- 6) Y. Yan, Z. Huang, X. Liu and D. Jiang: *J. Sol-Gel Sci. Technol.* **44** (2007) 81–85.
- 7) J. Li, Z. Y. Fu, W. M. Wang, H. Wang, S. H. Lee and K. Niihara: *Ceram. Int.* **36** (2010) 1681–1686.
- 8) M. Dolle, D. Gosset, C. Bogicevic, F. Karolak, D. Simeone and G. Baldinozzi: *J. Eur. Ceram. Soc.* **27** (2007) 2061–2067.
- 9) W. H. Jiang and K. Yatsui: *IEEE Trans. Plasma Sci.* **26** (1998) 1498–1501.
- 10) W. H. Hayt, Jr. and J. E. Kemmerly: *Engineering Circuit Analysis*, sixth ed., (Mcgraw-Hill; 2002).
- 11) S. I. Tkachenko, V. S. Vorob'ev and S. P. Malyshenko: *J. Phys. D Appl. Phys.* **37** (2004) 495–500.
- 12) Powder Diffraction File, Joint Committee on Powder Diffraction Standards, ICDD, USA, Card No. 00-035-0784 (2007).
- 13) C. Bernhardt: *Particle Size Analysis: Classification and Sedimentation Methods*, first ed., (London: Chapman & Hall; 1994).