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Generation and characterization of zirconium nitride nanoparticles by wire explosion process

R. Sugunakar Reddy [a,*], M. Kamaraj [b], U. Kamachi Mudali [c], S.R. Chakravarthy [d], R. Sarathi [a]

[a] Dept. of Electrical Engineering, IIT Madras, Chennai 600036, India
[b] Dept. of Metallurgical and Materials Engg., IIT Madras, Chennai 600036, India
[c] Corrosion Science and Technology Group, IGCAR, Kalpakkam, India
[d] Dept. of Aerospace Engg, IIT Madras, Chennai 600036, India

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Abstract

In the present study, wire explosion process (WEP) has been used to produce zirconium nitride (ZrN) nanoparticles. The produced ZrN nanoparticles were characterized through X-ray diffraction (XRD) and by the selected area electron diffraction (SAED) studies. The size and shape of the particles were analyzed using Transmission Electron Microscope (TEM). An analysis based on Log-normal probability distribution was used to quantify the particle size distribution of the powder. High speed photography was used to observe the wire explosion process.

Keywords: Nanoparticle; Zirconium nitride; Wire explosion; Log-normal distribution; XRD; TEM

1. Introduction

Nanoparticles often have good electrical, thermal, mechanical, chemical, optical, magnetic properties, etc., and materials scientists are challenged to identify, build, control, and test the nanostructured object, and to demonstrate the potential of these nano-structures in scientific, industrial or medical applications. By engineering size, shape, morphology and composition of the nanoparticles, the required characteristics of the nanostructured material could be achieved [1,2]. Zirconium nitride (ZrN) has good chemical and physical properties with high thermal stability, hardness, abrasive resistance and electrical conductivity [3,4]. It has many applications such as refractory material [5], hard coating for cutting tools [6] and Josephson junction in electronics [7]. Zirconium nitride particles were generated by various processes, which include, ball milling process [8], and benzene-thermal method [9]. Fu et al. [5] produced cubic phase zirconium nitride particles (in the range 30–100 nm) by reduction–nitridation of zirconium oxide powder (at 1000 °C for 6 h) in ammonia gas with magnesium as the reducing agent. Recently, Jiang and Yatsui [10] have demonstrated that it is possible to produce nanoparticles by wire explosion process and shown that it is a simplest and a cost-effective process. In the wire explosion technique, by providing proper energy to the conductor for evaporation and by maintaining suitable medium for nitridation, it is possible to generate nitride nanoparticles.

Having known all this, in the present work, a methodical experimental study was carried out to produce zirconium nitride nanoparticles of much lower size, by wire explosion process, by exploding zirconium conductor in a nitrogen atmosphere. The synthesized powders were characterized by X-ray diffraction (XRD) and by selected area electron diffraction (SAED) analysis. Size and shape of the particle formed by wire explosion process were analyzed by using transmission electron microscope (TEM). 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 nitrogen were analyzed.

2. Experimental details

The process of nanoparticle formation by wire explosion process includes conversion of solid conducting material to a

* Corresponding author. Tel.: +91 4422575465.
E-mail address: ee10d018@ee.iitm.ac.in (R. Sugunakar Reddy).

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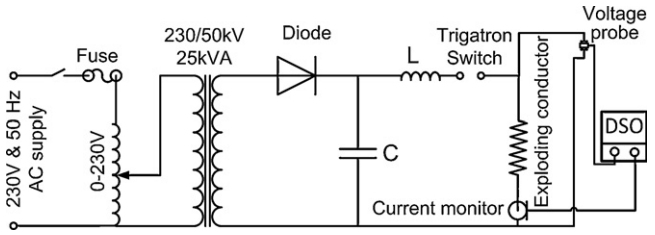

Fig. 1. Basic electrical circuit.

vapor state by injecting a high magnitude of current (of the order 10^8 A/cm^2) within a microsecond duration [11]. 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 of nanosized particles. Thus, the wire explosion process is basically a one step process for the generation of nanoparticles.

In the present work, the zirconium nitride particles were generated by wire explosion process, in which zirconium conductor was exploded in the nitrogen ambience.

Fig. 1 shows a basic circuit used for exploding the conducting wires to form nanopowders. Table 1 provides the details of the parameters used in the present study. The switch S 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. Energy stored in the capacitor is given by $W = (1/2)CV^2$ where, C is the capacitance of the capacitor and V is the charging voltage of the capacitor. By varying the charging voltage, it is possible to deposit the required energy. 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 capacitance of the capacitor (C), resistance of the exploding conductor (R), and the circuit inductance (L) [12]. In present work, circuit parameters match the condition for an under-damped RLC circuit, where

$$\frac{R^2}{4L^2} < \frac{1}{LC} \tag{1}$$

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

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

Table 1
Experimental details.

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

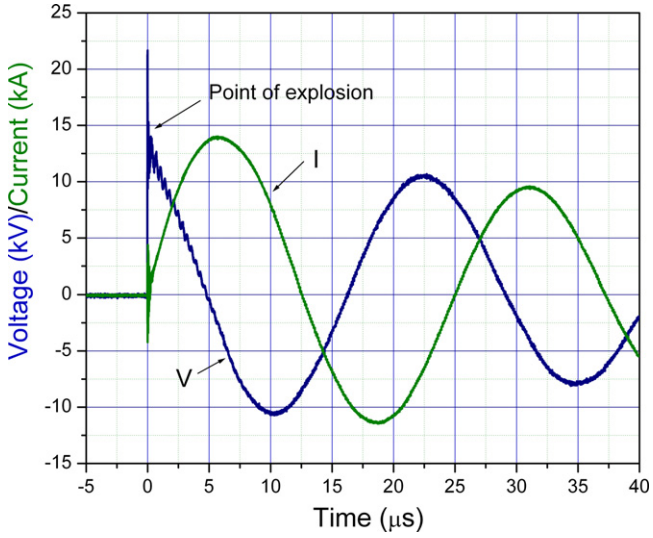

Fig. 2. Voltage and current waveforms during the explosion.

Fig. 2 is the applied voltage and the current waveforms measured during wire explosion process in nitrogen ambience. The applied voltage was measured at the input terminal of the exploding conductor using high voltage probe (EP-50K, PEEC.A, Japan). The current flow in the return conductor was measured using high bandwidth current transformer (Pearson Electronics, USA, CT Model No. 101), which is the current flow through the exploding conductor (up to the point of vaporization) and on vaporization forming plasma, thereby the plasma current continues to flow in the circuit.

At the point of explosion, a dip in magnitude of current followed with damping of current with oscillations is observed. The dip in magnitude of current at the point of explosion is due to increase in resistivity of the wire due to vaporization. The resistivity (φ) of the wire conductor vary with temperature (T) and density (γ) of the wire material and can be calculated as [13]

$$\varphi(\gamma, T) = \rho_0[1 + \theta(T - T_0)]\left(\frac{\gamma}{\gamma_0}\right) \tag{3}$$

where $\gamma = \gamma_0[1 - \alpha(T)(T - T_0)]$, γ_0 is the density at the melting temperature, θ is the temperature coefficient of resistivity and α is the thermal expansion coefficient. The feature of damping oscillation after current drop indicates that the resistance of the wire becomes low again, indicating that the wire is turned to a plasma state contributing continuous oscillatory current to flow even after physical absence of wire conductor [14,15]. In the present study, capacitance of the capacitor is 3 μF and summation of lead inductance in the circuit with internal inductance of capacitor is measured to be 5.3 μH, which is contributing to the frequency of oscillation of 40 kHz.

The amount of energy deposited to the wire conductor, up to the point of breakdown, has higher influence on the size of nanoparticles formed. 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/g. 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 1 to 3.

In present study, X-ray diffraction measurements were performed using (X'pert pro PANalytical) diffractometer with Cu-K_α radiation of wavelength 1.5425 Å. The particle size and morphology of the sample and the corresponding selected area electron diffraction (SAED) analysis was carried out by (Philips 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

Wire explosion process is basically an adiabatic process where the solid conducting wire is transformed directly to the vapor stage instantaneously by depositing energy sufficiently high for the solid wire to become vapor. Also, diameter of the conductor is chosen such a way that the current density is uniform to avoid layered vaporization [16]. Admittedly, the heat capacity of solid metal/in liquid state varies with temperature, which is a function of energy deposited to the conductor. For a metal wire with diameter d and length L, and current $I(t)$ is injected, the energy deposited to the conductor during time 't' is calculated as [17]

$$dE = I^2(t)\rho(T)\frac{L}{S}dt \tag{4}$$

where ρ is the electrical resistivity of the metal, and $S = \pi d^2/4$ is the wire area, and for solid and liquid state of the metal, the variation in temperature for the deposited energy can be calculated as

$$dT = \frac{dE}{mC_p(T)} \tag{5}$$

where C_p is the heat capacity at constant pressure, also we neglect the contribution of radiation in the energy balance.

Thus, it is possible to calculate deposited energy and rise in temperature with time. In the present study, on injection of high magnitude of current with short rise time, the rise in temperature causing solid to liquid to vapor state occurs in few microseconds. Hence in the present study, the energy deposition was calculated in simplified form, assuming the differential temperature between the room temperature to the point of melting and based on differential temperature between melting temperature and the temperature at the boiling point of liquid. Thus, minimum energy to be deposited should be equal to number of moles times the latent heat of vaporization of the metal conductor. Therefore, the energy required for vaporization of material W_s, in general can be calculated in simplified form as [18]

$$W_s = C_s \times \Delta T_m + h_v + h_m + C_f \times \Delta T \tag{6}$$

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 initial temperature, $\Delta T = T_b - T_m$, T_b is the final temperature, h_m is the

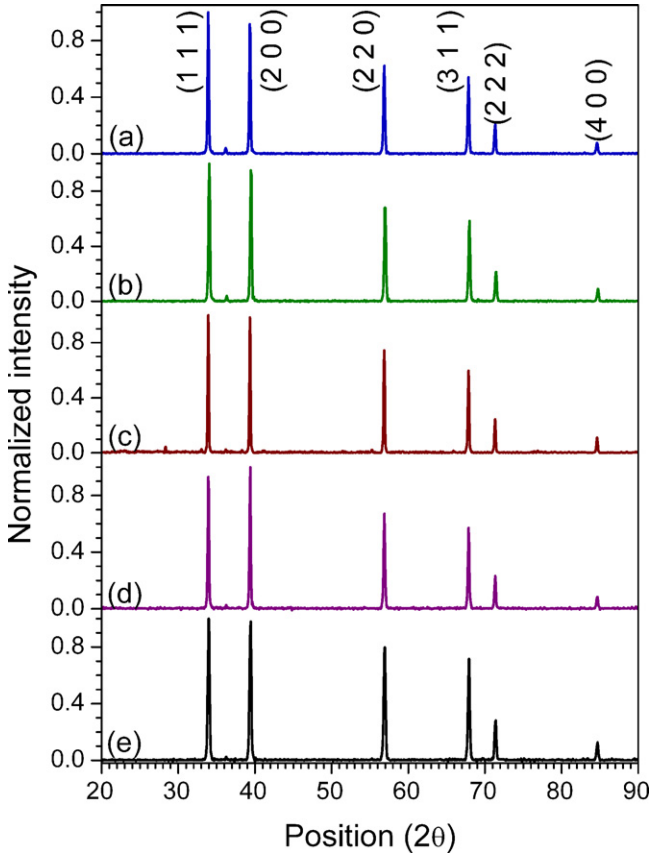

Fig. 3. XRD pattern of ZrN produced by wire explosion process in N_2 pressure at 100 kPa with (a) $W/W_s = 1$, (b) $W/W_s = 2$, (c) $W/W_s = 3$ and for $W/W_s = 3$ with (d) N_2 pressure at 50 kPa and (e) N_2 pressure at 25 kPa.

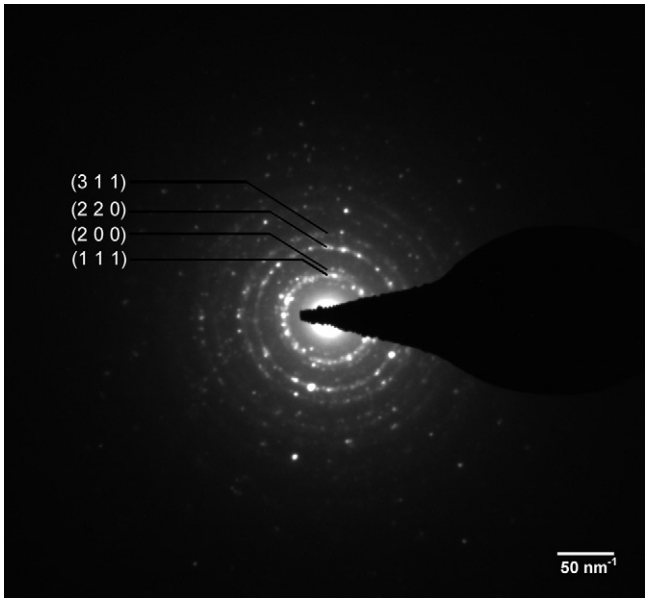

Fig. 4. Typical SAED pattern of zirconium nitride nanoparticle produced by wire explosion process with $W/W_s = 3$ in nitrogen ambience pressure of 100 kPa.

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 nitride nanoparticles were generated by exploding zirconium conductor in nitrogen ambience which acts as a nitriding agent. The vaporized zirconium metal nitrides due to nitrogen gas in the surrounding medium, which are at room temperature, allow nucleation of zirconium nitride particles. A stable equilibrium condition is

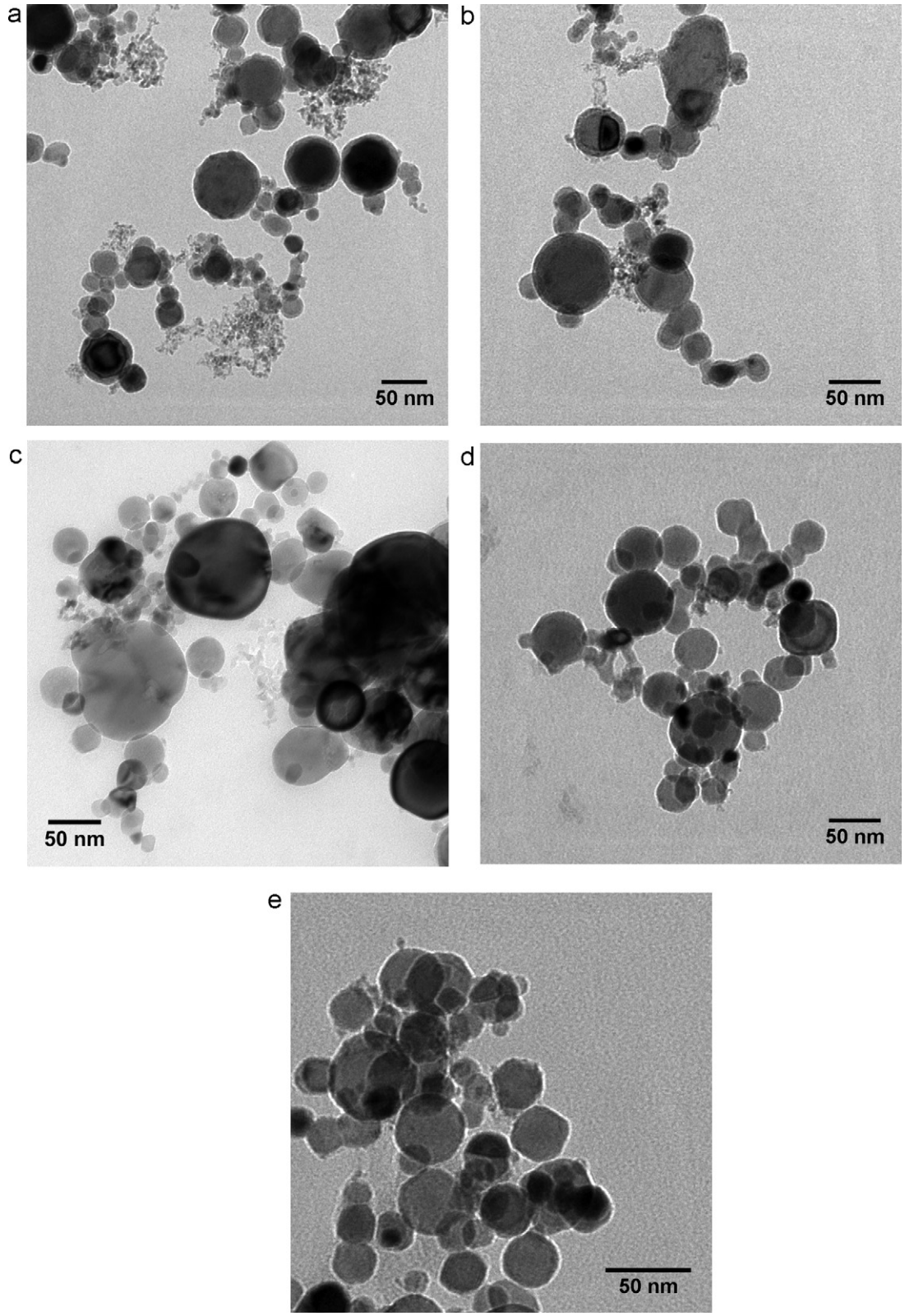

Fig. 5. TEM images of ZrN produced by wire explosion process in N_2 pressure at 100 kPa with (a) $W/W_s = 1$, (b) $W/W_s = 2$, (c) $W/W_s = 3$ and for $W/W_s = 3$ with (d) N_2 pressure at 50 kPa and (e) N_2 pressure at 25 kPa.

attained with the formation of new phase particles (nucleation). The particles formed further may coagulate or coagulate and condense to form nanoparticles depending on the local temperature. The zirconium nitride particles produced by wire explosion process was violet in color.

Fig. 3 shows XRD pattern of the zirconium nitride nanoparticles obtained by exploding zirconium conductor in nitrogen atmosphere at different pressure and by depositing different levels of energy. The XRD patterns indicate zirconium nitride characteristic diffraction peaks of 2θ at 33.89, 39.33, 56.83, 67.85, 71.31 and 84.61 [19], confirming that the particle produced by exploding zirconium conductor in nitrogen ambience produces zirconium nitride particles. It is also observed that, no sub nitride peaks were found. The analysis of the study also indicates no traces of zirconium oxide in the powder generated by the wire explosion process. Fig. 4 shows typical SAED pattern obtained for the zirconium nitride particle confirming that the particles produced by wire explosion process is Cubic structured Zirconium nitride [19].

Fig. 5 shows typical TEM pictures of zirconium nitride nanoparticles obtained by exploding zirconium conductor in nitrogen ambience (at different pressures) and by depositing different level of energy deposition. The synthesized zirconium nitride 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 [20] where,

$$f(d) = \frac{1}{\sqrt{2\pi} d \ \log \ \sigma_g} \exp\left(\left\{ - \frac{(\log \ d - \log \ D_{50})^2}{2(\log \ \sigma_g)^2} \right\} \right) \quad (7)$$

$$\sigma_g = \sqrt{\frac{\sum n_i (\log \ d_i - \log \ D_{50})^2}{\sum n_i}} \quad (8)$$

$$\log \ D_{5_0} = \frac{\sum n_i \ \log \ d_i}{\sum n_i} \quad (9)$$

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, respectively.

Fig. 6 shows the particle size distribution of the zirconium nitride nanoparticles produced by wire explosion process in nitrogen ambience (at different pressures) and by depositing different level of energy, respectively. The mean size of the particles calculated through distribution studies is shown in Table 2. Operating pressure of nitrogen gas and the amount of energy deposited to the exploding conductor during wire explosion process, have certain influence on the particle produced. Fu et al. generated zirconium nitride nanoparticle by nitridation of zirconium oxide particles and have produced particles of size 40 nm [5]. In the present study, it is observed that increase in operating pressure shows a marginal reduction in size of the particle, 10 nm. 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 10 nm zirconium nitride particles could be produced by wire explosion process, in single step process without any further processing.

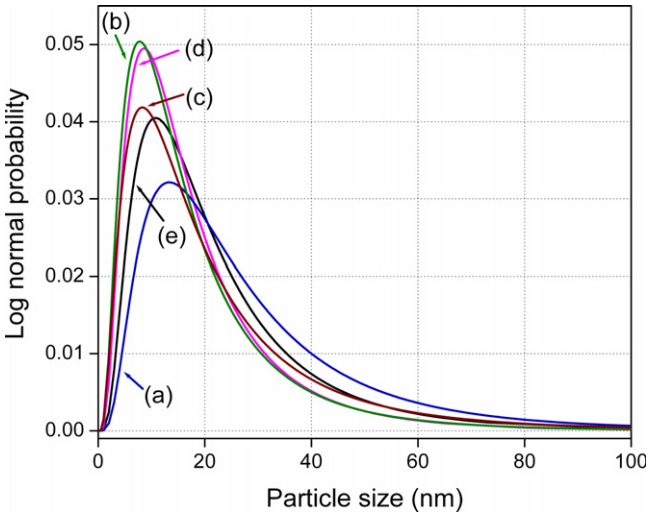

Fig. 6. Particle size distribution of ZrN produced by wire explosion process in N_2 pressure at 100 kPa with (a) $W/W_s = 1$, (b) $W/W_s = 2$, (c) $W/W_s = 3$ and for $W/W_s = 3$ with (d) N_2 pressure at 50 kPa and (e) N_2 pressure at 25 kPa.

Table 2
Variation in mean diameter and geometric standard deviation of the zirconium nitride particles.

(a) Produced for $W/W_s = 3$ in N_2 ambient at various pressures

Pressure (kPa)	Geometric mean (D_{50}, nm)	Geometric standard deviation
25	17.86	2.03
50	14.49	2.06
100	16.27	2.27

(b) Produced for various W/W_s ratios in N_2 ambient at 100 kPa pressure

W/W_s ratio	Geometric mean (D_{50}, nm)	Geometric standard deviation
1	22.36	2.05
2	13.90	2.14
3	16.27	2.27

Fig. 7 shows typical photographs obtained by high speed camera during wire explosion process. It is observed from high speed camera images that nanoparticle formation by wire explosion process can extend up to few milliseconds. Subfigure in Fig. 7(a) shows the image of the conductor wire, before explosion. On injection of high current, explosion of conductor occurs in few seconds and only a white bright light is observed at that instant (Fig. 7a). It is well known that on vaporization, by exchange of heat to the ambient medium, nucleation of particle occurs followed with coagulation/condensation/agglomeration of nucleated particle to form particles of different size. Based on the images obtained through high speed camera, it is evident that the formation of Zr nanoparticle occurs by exploding the zirconium conductor in helium ambience, the process is completed in 1.1 ms (Fig. 7c). On explosion of zirconium conductor in nitrogen ambience, nanoparticles of zirconium nitride is formed and the process extends up to 2 ms (Fig. 7d) indicating that localized reaction occurs in the medium to form

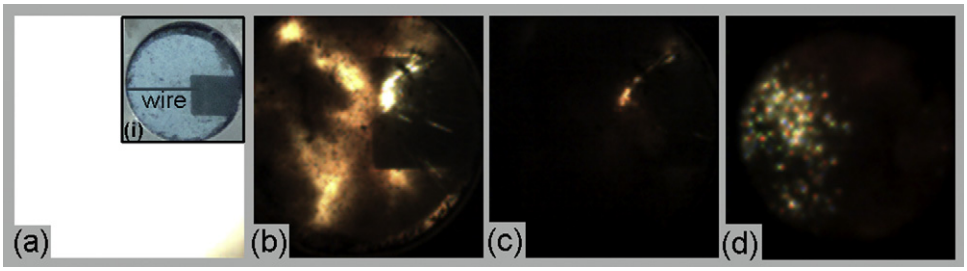

Fig. 7. Typical photograph obtained during wire explosion process in He ambience at (a) 0.1595 ms (b) 0.8 ms (c) 1.1 ms and at (d) 1.8 ms of Nitrogen ambience.

zirconium nitride. Thus, it is possible to conclude that zirconium nitride formation process is little longer than the zirconium particle formation, through high speed photography.

4. Conclusions

The zirconium nitride nanoparticles were produced by wire explosion process by exploding zirconium conductor in nitrogen ambience. XRD studies and SAED patterns confirmed the formation of zirconium nitride particle. No traces of zirconium oxide were found in the XRD pattern of the zirconium nitride powders produced. It has been observed that crystallite size of the particle produced by wire explosion process is 10 nm. TEM analysis has shown that zirconium nitride 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 nitride particles produced by wire explosion process was less than 20 nm. High speed photography was used to observe the wire explosion process and could conclude that the duration of ZrN particle formation takes longer time than the Zr metal particle formation.

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