Size Tailored Nanoparticles of ZrN Prepared by Single-Step Exothermic Chemical Route

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Abstract ZrN nanoparticles were prepared by an exothermic reduction of $ZrCl_4$ with NaN_3 in the presence of NaCl flux in a nitrogen atmosphere. Using a solid-state combustion approach, we have demonstrated that the zirconium nitride nanoparticles synthesis process can be completed in only several minutes compared with a few hours for previous synthesis approaches. The chemistry of the combustion process is not complex and is based on a metathesis reaction between $ZrCl_4$ and NaN_3 . Because of the low melting and boiling points of the raw materials it was possible to synthesize the ZrN phase at low combustion temperatures. It was shown that the combustion temperature and the size of the particles can be readily controlled by tuning the concentration of the NaCl flux. The results show that an increase in the NaCl concentration (from 2 to 13 M) results in a temperature decrease from 1280 to 750°C. ZrN nanoparticles have a high surface area (50-70 m²/g), narrow pore size distribution, and nano-particle size between 10 and 30 nm. The activation energy, which can be extracted from the experimental combustion temperature data, is: $E = 20$ kcal/mol. The method reported here is self-sustaining, rapid, and can be scaled up for a large scale production of a transition metal nitride nanoparticle system (TiN, TaN, HfN, etc.) with suitable halide salts and alkali metal azide.

Key words zirconium nitride, nanoparticles, combustion synthesis, particle size, sodium chloride.

1. Introduction

Zirconium Nitride (ZrN) is one of the hardest coating material and its unique characteristics, such as extreme hardness, good electrical conductivity, excellent thermal properties, wear, chemical and corrosion resistance, good lubricity and ductility make this material unchangeable for extending life of cutting tools, punching and forming dies, and wear components. Materials coated include most metals, ceramics, and some plastics. ZrN thin films can be applied to metal base transistors and three-dimensional integrated circuits since it can be grown epitaxially on Si. Due to its shiny and golden appearance, it can be used in the jewelry industry. With this regard the cost-effective synthesis of nanoscale zirconium nitride particles is technologically attractive and ZrN powder itself can be used for thermal plasma spraying to make uniform protective coating.¹⁾

Several approaches were reported for synthesizing ZrN nanopowders. Among them the followings can be noted: reduction-nitridation reaction,²⁾ benzene-thermal synthesis,³⁾ pulsed wire discharge synthesis⁴⁾ high-energy ball milling,⁵⁾

microwave plasma synthesis⁶⁾ and solid-state metathesis reaction.⁷⁻¹¹⁾ In reduction-nitridation method²⁾ nanocrystalline ZrN powder was synthesized from nanosized ZrO_2 powder in ammonia gas with magnesium as the reducing agent. Cubic phase ZrN powder with a 30-100-nm particle size was obtained at 1000°C for 6 h, under a Mg: ZrO_2 mole ratio of 10:1. In benzene-thermal synthetic route³⁾ a stainless steel autoclave containing anhydrous zirconium tetrachloride ($ZrCl_4$), lithium nitride (Li_3N) was heat treated at a temperature of 380-400°C to produce ZrN nanopowder. As-prepared ZrN powder exhibits cubic crystal shape and average particle size was estimated to be about 180 nm in diameter. In pulsed wire discharge method reported in⁴⁾ ZrN nanoparticles were synthesized by explosion of Zr wire in nitrogen. The results of measurement revealed the average particle sizes in the range of 20-70 nm. High-energy ball mill technique⁵⁾ a mixture of $ZrCl_4$ and Li_3N powders was milled in a high-energy ball mill under Ar atmosphere. After the extraction of LiCl from the final product, c-ZrN nanoparticles with an average diameter of 40 nm was obtained. In microwave plasma synthesis technique⁶⁾ $ZrCl_4$ was used as a precursor material and hydrogen was used as carrier gas. $ZrCl_4$ was evaporated in the heater and the vapor was injected uniformly into the plasma reaction region where it reacts with nitrogen

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radicals to form ZrN nanoparticles. Average particle size was in 10–40 nm intervals versus flow rates of carrier gas. In the solid-state metathesis reactions^{7–11)} anhydrous metal chloride MCl, and Ba₃N₂ (or Sr₃N₂, NaN₃) were ground together in an agate pestle and mortar in a nitrogen or argon filled glove box and then placed in a quartz or Pyrex ampoule which was evacuated and sealed. The ampoule was placed in an oven at 250–550°C for between 1 min and 10 h and allowed to cool to room temperature for typically 1–2 h. The ampoule contained a fused black solid which identified as nitride phases. However, most of the techniques described above produce ZrN nanoparticles larger than 20 nm. Moreover, these techniques have some disadvantages, such as low production rate (milligrams), long period of treatment and complicated experimental procedure.

In this study, we report a metathesis combustion reaction for the synthesis of extra-small size ZrN nanoparticles (less than 10 nm), using exothermic reduction of ZrCl₄ with NaN₃ in the present of NaCl flux. The control of the combustion temperature and ZrCl₄ evaporation process was reached throw application of an inert gas pressure and sodium chloride flux. The method reported in here is self-sustaining, rapid and could be scaled up for a large scale production of ZrN nanoparticles.

2. Experimental Procedure

Zirconium tetrachloride (ZrCl₄) powder (99.0% purity, Aldrich, USA), sodium azide (NaN₃) powder (99.0% purity, particle size < 50 µm, Daejung Chemical and Metals Co., Ltd., South Korea) and sodium chloride (NaCl), (98.5% purity, particle size 50–150 µm, Daejung Chemical and Metals Co., Ltd., South Korea) were used in the experiments.

A simplified scheme of the combustion process used

Fig. 1. A simplified scheme of the combustion process used for the experiments: A-initial components; B- reaction sample before (1), during (2) and after the combustion process (3); C-sample purification into glass beaker; (D)-ZrN nanopowder.

for the experiments is shown in Fig. 1. For the reaction mixture a controlled amount of reactant powders, ZrCl₄, NaN₃ and NaCl were weighed and thoroughly mixed in a glove box under argon atmosphere. From 80 to 100 gram mixture was hand compacted into stainless still cup (4.0 cm in diameter) and placed into a high-pressure reaction vessel for the combustion experiment. The combustion process was initiated by a hot nickel-chromium filament system under 2.0 MPa nitrogen pressure. Reaction temperatures were measured using WR-20/WR-5 thermocouples inserted in the reaction pellet. After the completion of the combustion process, the burned down sample was cooled down to room temperature and transferred to a 500-ml beaker for further purification. This sample was purified via washing with distilled water in order to remove the NaCl. Purified black powder was dried under the vacuum at 40–50°C.

We used “HSC Chemistry 6” software to predict adiabatic combustion temperature (T_{ad}) and concentration of equilibrium phases in the combustion wave.¹²⁾ The calculation of equilibrium characteristics was based on minimizing the thermodynamic potential of the system. The initial parameters (temperature and pressure) of the system were set to 25°C and 2.0 MPa, respectively. The analysis was performed under a NaCl concentration of 2–13 M.

The crystal structure and morphology of the ZrN nanoparticles were characterized using an X-ray diffractometer with Cu K α radiation (Siemens D5000, Germany), field emission scanning electron microscopy (FESEM; JSM 6330F) and transmission electron microscopy (TEM, JEM 2010, Japan). The specific surface area was determined from the linear part of the BET plot. The micropore size distribution was calculated by using the adsorption branch of the N₂ adsorption-desorption isotherm.

3. Results and Discussion

Fig. 2. shows the adiabatic combustion temperature (T_{ad}) and equilibrium phases for the ZrCl₄ + 4NaN₃ + k NaCl system. Thermodynamic analysis indicates that adiabatic combustion temperature calculated for $k=0$ is about 1656°C. This result may lead to an intensive evaporation of ZrCl₄ ($T_{evap.} = 331^\circ\text{C}$) during the combustion process, even under 2.0 MPa pressure. Therefore, NaCl was employed as effective diluent to decrease the adiabatic combustion temperature. It is noteworthy that the response of T_{ad} to the NaCl concentration is very effective; the decrease in the temperature is about 100°C per each mol of NaCl. Therefore at $k=8$ the overall system temperature drops to the melting point of NaCl (800°C). Further increase in k ($k > 8$) affects on the proportion of NaCl(s)/NaCl(l), while T_{ad} remains constant. Reaction products assumed by the thermodynamic analysis consists of two main phases,

Fig. 2. Thermodynamic analysis of $\text{ZrCl}_4\text{-4NaN}_3\text{-}k\text{NaCl}$ system.

solid ZrN and water soluble NaCl. In the given condition, NaCl can be in liquid, solid, or gaseous states depending on processing temperature. Thus, thermodynamic analysis indicates that the control of the temperature by NaCl flux is attractive and under the given thermodynamic circumstances the synthesis of ZrN nano particles seems to be realistic.

The experimental conditions were employed for the thermodynamic analysis. Preliminary tests in $\text{ZrCl}_4 + \text{NaN}_3$ binary system revealed that essential evaporation of ZrCl_4 during the combustion process occurred. Starting with 2 M of NaCl, the combustion process in $\text{ZrCl}_4 + \text{NaN}_3$ system is thermodynamically stabilized and loss in mass of sample is negligible. Reaction temperature profiles at different NaCl concentrations (k) are shown in Fig. 3(a). All profiles exhibit a single-stage character with an abrupt temperature increase in the beginning part of the reaction zone. The ignition point (T^*) of $\text{ZrCl}_4 + 4\text{NaN}_3 + k\text{NaCl}$

Fig. 3. Temperature-time profiles (a) and combustion parameters (b) of $\text{ZrCl}_4\text{-4NaN}_3\text{-}k\text{NaCl}$ system upon k .

Fig. 4. XRD patterns of $\text{ZrCl}_4\text{-4NaN}_3\text{-}k\text{NaCl}$: (a) $k=2$; (b) $k=5$; (c) $k=8$ and (d) $k=13$.

system defined by inflection point of temperature profiles is located between 300–400°C where a thermal decomposition of NaN_3 (280–300°C) and boiling of ZrCl_4 (331°C) take places. In this point, any visible change in T^* from k was observed in Fig. 3(a). However decrease in the combustion temperature (T_c) and velocity (U_c) upon k is essential. As shown in Fig. 3(b) the combustion temperature decrease from 1280 to 750°C in 2–13 range of k . Combustion wave velocity also displays a continuously retarded characteristic with reaching to the minimum value (0.15 cm/s) at $k=13$.

X-ray diffraction patterns of water purified combustion products upon k are shown in Fig. 4. As depicted, at 1280°C ($k=2$) all XRD peak is well matched to ZrN phase. With increasing of k the intensities of ZrN peaks are continuously decreased, simultaneously ZrO_2 impurity peaks are appeared on patterns. At $k=13$ the XRD peaks of ZrN become very weak; it imply that the powder is getting quasi-amorphous.

SEM micrograph of the sample after the combustion process (Fig. 5A) shows large volume of molten NaCl in which the small particles of ZrN are randomly distributed. The reaction sample after water purification was transformed to a homogeneously colored black powder as shown in Fig. 5(B). This powder is somewhat agglomerated and the size of agglomerates is less than 1 μm .

Typical TEM (A, B), high-resolution cross-sectional TEM image (C), and electron diffraction pattern of ZrN nanopowder (D) are shown in Fig. 6. Fragments A and B represent the TEM images of ZrN nanopowders prepared with 2 and 8 M of NaCl. With 2 M of NaCl the average size of particles is about 30 nm, whereas 8 M of NaCl may produce ZrN particles with average size less than 10 nm.

Fig. 5. SEM fragment from the combusted sample (A); ZrN powder after the purification and its SEM morphology (B).

Fig. 6. Typical TEM (A, B), high-resolution cross-sectional TEM image (C) and SAD diffraction pattern of ZrN nanopowder (D).

Fig. 6(C) high resolution transmission electron microscopy (HRTEM) images further support the interplanar distances of $d = 2.65 \text{ \AA}$ which is identical with the plane $d_{220} = 2.65 \text{ \AA}$. Fig. 6(D) shows the selected area diffraction (SAD) pattern of ZrN, which is in exact/or in good agreement with the XRD results. The ring type SAD pattern consists of a NaCl type cubic structure and it indicates the ultrafine character of ZrN nanoparticles. And also, diffraction ring from (220) of ZrO_2 is dimly visible, which represents the inclusion of small amount of ZrO_2 . Taken together, the results of XRD, TEM and HRTEM, show that the synthesized ZrN nanoparticles are in range of 5–30 nm and it can be crystalline or quasi-amorphous depending on the reaction temperature.

Fig. 7. (a) N_2 adsorption-desorption isotherm and (b) HK pore-size distribution plot of ZrN nanopowder.

The surface area and porosity of the ZrN nanoparticles were investigated by using Brunauer-Emmett-Teller (BET) analysis and the nitrogen adsorption-desorption isotherm. Because the ZrN nanoparticles were small, a high surface

area was expected, which is also verified from results of the BET analysis. The BET specific surface area was from 50.27 to 70.15 m²/g. Fig. 7(a) shows the adsorption/desorption isotherms of nitrogen measured at liquid nitrogen temperature (77.3 K). Here, p/p^0 is relative pressure, and V_a is volume of adsorbed and desorbed amount of N₂. A hysteresis loop can be observed between the adsorption and desorption branch indicating the porous structure of zirconium nanoparticles. The ZrN nanoparticles showed a type II isotherm according to the IUPAC classification.¹³⁾ There were sharp increases at $P/P_0 < 0.05$ and $P/P_0 > 0.9$, as shown in Fig. 7(a). The inflection position at $P/P_0 = 0.05$ -0.5 was due to the presence of primary mesopores, whereas the second increase at $P/P_0 > 0.9$ arose from capillary condensation with multilayer adsorption onto the inner surface. Fig. 7(b) shows the Horvath-Kawazoe (HK) pore volume-diameter distribution plots for N₂ at 77.3 K. The plot revealed that the ZrN nanoparticles possessed porous structures with a size distribution of 1-10 nm, the average pore diameter (d_p) of the zirconium was 9.29 nm, and the corresponding BET cumulative pore volume ($dV_p/d\log dp$) was 0.195 cm³/g.

Chemistry of the combustion process is not complex and it is based on the metathesis reaction between ZrCl₄ and NaN₃. Because of low melting and boiling points of raw materials it was possible to synthesized ZrN phase at low combustion temperatures. Generally the formation process of ZrN nanoparticles proceeds with participation of solid, liquid and gas phases and entire synthesis process may be presented by following sequential chemical reactions:

I stage (300-400°C):

II stage (750-1300°C)

As shown in Fig. 3, the ignition point of ZrCl₄-NaN₃ mixture is low (300-400°C), and therefore a low activation energy is needed for activation of the combustion process. According to the concept of wide reaction zones developed by Merzhanov¹⁴⁾ the combustion velocity is connected with the combustion temperature by the following equation:

$$U^2 = AT_c e^{-E/RT_c} \quad (5)$$

It is obvious that the activation energy for the combustion process can be derived from the experimental values U_c and T_c in Eq. (5). For it the values of T_c and U_c were processed in coordinates $\ln U_c/T_c - 1/T_c$. The results are presented graphically in Fig. 8. The activation energy which

Fig. 8. Activation energy of ZrCl₄-4NaN₃-kNaCl system (K = 2~13).

can be extracted from the plot is: $E = 20$ kcal/mol.

4. Conclusion

A combustion approach has been developed to produce ZrN nanoparticles from ZrCl₄-4NaN₃ mixture diluted with NaCl flux. Thermodynamic and kinetic analysis through the in situ measurement of the sample temperature indicates that the combustion reaction has high exothermicity and may develop a temperature from 1280 to 750°C with increasing the flux concentration from 2 to 13 M. The calculated effective value for activation energy in this process is 20 kcal/mol. The average size of ZrN particles under the given circumstances was decreased from 30 nm to 10 nm (or less) with increasing NaCl concentration. ZrN nanoparticles have high surface area (50-70 m²/g) and narrow pore size distribution (1-10 nm). This synthetic method can be easily applied for other transition metal nitride systems (TiN, TaN, HfN, etc.) with suitable chloride salts and alkali metal azide.

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