A Benzene-Thermal Synthetic Route to Nanocrystalline ZrN

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Nanocrystalline ZrN has been successfully prepared via benzene-thermal reaction of $ZrCl_4$ and NaN_3 at 350-380 °C. X-ray powder diffraction patterns indicated that the crystallinity of ZrN was considerably high and the cell constant was a = 4.567 Å. Transmission electron microscopy images showed the powders consist of uniform spherical particles with a narrow particle-size distribution (10-20 nm). The role benzene-solvent played in the formation of nanocrystalline ZrN was discussed.

Transition-metal nitrides have considerable interest because of special properties such as extreme hardness, high temperature stability, and excellent conductivity.[1] They are found uses as hard, protective coatings for cutting tools and UHV system components.[2-4] Dense crucibles of ZrN and TiN have served as vessels for the melting of metals.[5] Conventionally, transition-metal nitrides have been made at high temperature (>1000 °C) by the reaction of ammonia or dinitrogen with the pure metal or metal hydride.[6] A number of process exist for synthesizing transition-metal nitrides. For examples, low-energy chemical molecule precursor routes, solid-state metathesis (SSM) routes, and solid-liquid metathesis reactions have been demonstrated for synthesis of transition-metal nitrides powders.[7-9] Most of these reactions involve processing temperature higher than 1000 °C for extended time periods, which result in the grain growth and agglomeration of the powders. Recently. Parkin has reported the thermal initiation of reactions between sodium azide and metal chlorides to binary metal nitrides at lower temperature than conventional synthetic pathways.[10] However, the crystallinity of products obtained from the route is considerably low.

In this letter, we report a benzene-thermal reaction of $ZrCl_4$ and NaN_3 in which benzene was used as a solvent to synthesize nanocrystalline ZrN with higher crystallinity. The reaction was carried out in an autoclave at 350-380 °C and can be represented by eqn:

$$ZrCl_4 + 4NaN_3 \xrightarrow{\text{benzene}} ZrN + 4NaCl + 11/2N_2$$

The solvent of benzene can absorb the reaction enthalpy released from this process and maintain a relative low overall reaction temperature. This is beneficial to the formation of nanocrysatlline ZrN.

All manipulations were carried out in a dry glove-box filled with flowing N_2. In a typical procedure, an appropriate amount of analytical grade $ZrCl_4$ (4.5 g) and NaN_3 (5.0 g) were put into a titanium alloy autoclave of 50 mL capacity and then the autoclave was filled with 40 mL benzene. After sealed, the autoclave was maintained at 350-380 °C for 8 h, and then allowed to cool to room temperature. The precipitate was collected, filtered off, and washed with 0.1 M hydrochloric acid, distilled water, successively. The product was dried in a vacuum at 70 °C for 1 h and the final powder was obtained.

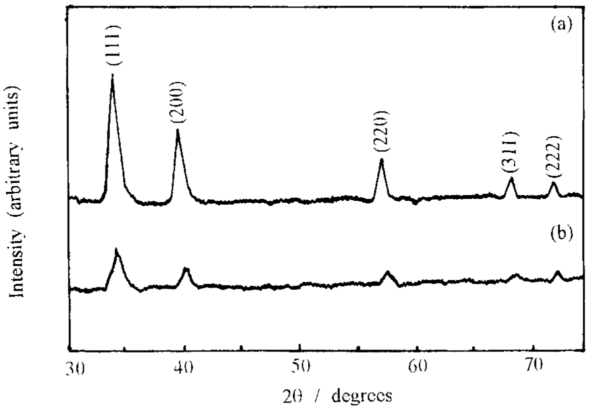

Figure 1. XRD patterns of ZrN sample (a) prepared via a benzene-thermal reaction of $ZrCl_4$ with NaN_3 at 360 °C for 8 h in an autoclave and (b) prepared from the solid-state reaction of $ZrCl_4$ with NaN_3 at 360 °C for 8 h in an autoclave.

The samples were characterized by X-ray powder diffraction (XRD) method, operating on a Japan Rigaku Dmax-γA X-Ray diffractometer with graphite-monochromatized Cu $K\alpha$ radiation (λ = 1.5418 Å). Figure 1(a) shows the XRD pattern of as-prepared ZrN sample by a benzene-thermal route. All reflections could be indexed to be the cubic phase ZrN with cell constant a = 4.567 Å, in accordance with the reported values in literature (a = 4.7756 Å).[11] No impurities such as metallic Zr or ZrO_2 were detected in Figure 1(a). The characteristic XRD peaks broadening is due to very fine grain size. Using the Scherrer equation, the calculated grain size was 20 nm. Figure I (b) shows the XRD pattern of ZrN sample from a thermal initiation (360 °C) of reaction between $ZrCl_4$ and NaN_3 on the same molar scale in the autoclave. It can be seen the ZrN from solid state reaction of $ZrCl_4$ and NaN_3 is considerably lower crystalline.

Transmission electron microscope (TEM) images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Figure 2(a) shows the TEM image of the ZrN nanocrystallines through a benzene-thermal route. It can be seen that the powders consist of uniform spherical with loose agglomeration and the sizes of the particles are in the range of 10-20 nm in diameter. Figure 2(b) shows the TEM image of the ZrN powders from the solid state reaction. It can be seen that the powders display a disklike morphology and the sizes are in the range of 30-80 nm in diameter.

The influences of reaction temperature and time on the formation of nanocrystalline ZrN were investigated. An optimum reaction conditions for the formation of nanocrystalline ZrN was 350-380 °C for 8 h. Although the thermally initiated

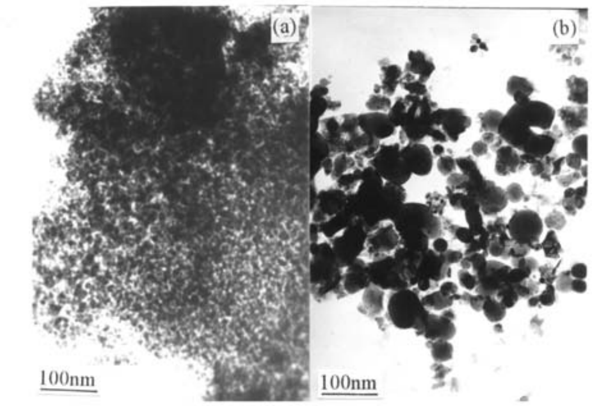

Figure 2. TEM images of ZrN sample (a) prepared via a benzene-thermal reaction of $ZrCl_4$ with NaN_3 at 360 ℃ for 8 h in an autoclave and (b) prepared from the solid-state reaction of $ZrCl_4$ with NaN_3 at 360 ℃ for 8 h in an autoclave.

solid state reaction of $ZrCl_4$ with NaN_3 to form ZrN is exothermic, in our benzene-thermal route, nanocrystalline ZrN cannot be obtained at a temperature up to 330 °C (a thermal decomposition temperature of NaN_3).[12] If the reaction time was shorter than 4 h at a suitable temperature, for example, 360 °C, the reaction was incomplete and the crystallinity of ZrN was lower. If the temperature was higher than 400 °C, or the time was longer than 12 h, the particles size increased. Furthermore, the product obtained was contaminated by the carbonization of benzene.

Conventional initiation of the reactions between sodium azide and metal chlorides are typical exothermic.[13] In most cases, the reactions are almost instantaneous, and proceed with a visible thermal flash. The products obtained were a fused mass rather than an ultrafine powder and the crystallinity of products was considerably low.[10] In our present route, the benzene-solvent can absorb the reaction enthalpy released from this process and maintain a relative low overall reaction temperature. So, the products prepared were nanosized rather than fused. Meanwhile, ZrN nanocrystalline may be produced through a liquid-solid-solution reaction. This route thus differs substantially from solid state reactions, which require to overcome the large diffusion distance associated with the reactant particles. Therefore, the crystallinity of nanocrystalline ZrN from the present route was considerably higher than that obtained from the comparable solid state reaction of $ZrCl_4$ and NaN_3 (as shown in Figure 1).

The thermal decomposition of NaN_3 is known to proceed according to the overall equation: $2NaN_3 \rightarrow 3N_2 + 2Na$ [12]. A previous report on the details of the reaction indicated that nitrogen atoms can be generated from this decomposition process.[14] In our benzene-thermal route, we may prefer a reduction-nitridation route to ionic metathesis pathway to ZrN. The formation process might be illustrated as follows:

$$N_3^- \rightarrow N_2 + N + e + \text{energy} \qquad (2)$$

$$Na^+ + e \rightarrow Na \qquad (3)$$

$$ZrCl_4 + 4Na \rightarrow Zr + 4NaCl + \text{energy} \qquad (4)$$

$$Zr + N \rightarrow ZrN \qquad (5)$$

In this route, the hot benzene-solvent in the autoclave can act as a transition medium of nitrogen atomic and electron of the system.

In summary, nanocrystalline ZrN has been successfully prepared via a benzene-thermal reactions of $ZrCl_4$ and NaN_3. The benzene-solvent plays an important role in the formation for nanocrystalline ZrN. This present method allows the fabrication of ZrN powders with higher crystallinity and a narrow particle-size distribution and loose agglomeration. The present solvothermal synthetic route may be extended to prepare other nanocrystalline metal nitrides.

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