Solid-state synthesis of zirconium nitride and hafnium nitride powders

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Zirconium nitride (ZrN) powders have been prepared by using the zirconium dioxide (ZrO₂), sodium azide (NaN₃) and metallic magnesium (Mg) as starting materials in a stainless-steel autoclave. The X-ray powder diffraction pattern indicates the formation of cubic phase ZrN. Hafnium nitride (HfN) can also be synthesized from hafnium dioxide (HfO₂) through the similar procedure.

Key-words : Nitride, Chemical synthesis, Powders, X-ray diffraction

Transition metal nitrides are key industrial materials for their excellent properties such as high melting point, good abrasive resistance, high hardness, good electrical and thermal conductivity, and remarkable chemical resistance. Among the transition metal nitrides, zirconium nitride (ZrN) can be used as wear resistant coating on the cutting tools for its high hardness (~15 GPa). Moreover, zirconium nitride can also be used as refractory and superconducting materials.

Over the past decade, several different methods for the preparation of zirconium nitride have been reported. Fei et al. have synthesized ZrN nanopowders by using ZrCl₄ and ZrOCl₂·8H₂O as zirconium source via soft urea pathway at 1673 K. ZrN can also be prepared via carbothermal reduction and nitridation of zircon sand (ZrSiO₄) through transferred arc plasma process. Li et al. have synthesized ZrN fibers by using electrospun PVP/zirconium oxychloride composite fiber as raw materials via carbothermal reduction and nitridation process at 1873 K. ZrN powders have been synthesized from the mechanochemical reaction of zirconium tetrachloride and lithium nitride. ZrN nanopowders have been synthesized via magnesium thermal reduction nitridation of ZrO₂ in a molten salt environment. Aluminum can also be employed as reductant to react with ZrO₂ to synthesize ZrN nanopowders under nitrogen pressures. ZrN and HfN powders have been synthesized by solvothermal reactions of metal chlorides and LiNH₂ in organic solvents. Hector and his co-workers have prepared transition metal nitrides (TiN, ZrN, and HfN) using solid state metathesis reactions of metal halides and lithium nitrides. ZrN powders can also be obtained by combustion reaction of metallic Zr and solid nitrogen sources (BN and Si₃N₄). Karaballi and his colleagues have reported the solid-state synthesis of titanium subgroup of metal nitrides (TiN, ZrN and HfN) nanoparticles from corresponding metal oxides (TiO₂, ZrO₂ and HfO₂) and magnesium nitride.

Carbothermal nitridation of zirconia is the most commonly chosen route to the production of ZrN, which has been done on an industrial scale using zirconia as raw material to reduce cost. However, the method usually requires high temperature (1973–2373 K) and long reaction time, and thus the synthesis of zirconium nitride from zirconia at low temperature is of great significance.

In this paper, zirconium nitride powders have been synthesized by the magnesium thermal reduction process. The reaction used in our approach can be expressed as follows:

\[ 2\text{Mg} + \text{NaN}_3 + \text{ZrO}_2 \rightarrow 2\text{MgO} + \text{ZrN} + \text{Na} + \text{N}_2 \]

This method can be extended to synthesize hafnium nitride. In a typical experiment, zirconium dioxide (ZrO₂, 0.32 g), sodium azide (NaN₃, 3.20 g), and excess metallic magnesium (Mg, 1.20 g) were loaded into a 20-mL stainless steel autoclave. The autoclave was sealed and heated from room temperature to 1273 K with a rate of 10 K/min in a resistance furnace and kept at 1273 K for 36 ks. After the autoclave was naturally cooled to room temperature,
the black product was collected from the autoclave. The obtained product was washed with dilute HCl, distilled water, and alcohol for several times to remove the by-product and excess un-reacted magnesium. Finally, the as-obtained products were dried at 323 K under vacuum for further characterization.

The phase analysis of the obtained product was examined by X-ray powder diffraction (Philips X’Pert diffractometer, Cu-Kα radiation). The microstructure of the obtained product was examined by a field emission scanning electron microscopy (FE-SEM, JEOL-JSM-6700F) and transmission electron microscopy (TEM, JEOL-2010). The high-resolution transmission electron microscope image was taken on a JEOL-2010 TEM with an accelerating voltage of 200 kV.

The X-ray diffraction (XRD) pattern of the as-prepared ZrN product is analyzed by XRD and shown in Fig. 1. Five diffraction peaks can be observed in Fig. 1. All of the five diffraction peaks with strong diffraction intensity could be indexed as the (111), (200), (220), (311), and (222) diffraction planes of face-centered ZrN with a lattice parameter \(a = 4.5734\) Å, which is in good agreement with the reported value for cubic ZrN \(a = 4.5745\) Å, JCPDS card no. 89-3839.

The morphology of the as-prepared ZrN product is further investigated by FE-SEM and TEM. The FE-SEM image and TEM image of the as-prepared ZrN are shown in Figs. 2(a) and 2(b). We find that the as-prepared ZrN sample is composed of particles with sizes ranging from 100 to 500 nm. The ZrN particles are agglomerated as in Fig. 2(b). As shown in Fig. 2(b), the average size of the ZrN powder is about 150 nm. The HR-TEM image of the as-prepared ZrN sample is shown in Fig. 2(c). From the HR-TEM image, the lattice spacing is measured to be 0.26 nm, which corresponds to (111) plane in cubic ZrN. The above result is consistent with the XRD conclusion.

XRD patterns of the products obtained at 973, 1073, and 1173 K are shown in Figs. 3(a)–3(c), respectively. All the diffraction peaks in Fig. 3(a) can be indexed to monoclinic phase ZrO₂ (JCPDS card no. 78-1807). The diffraction peaks in Figs. 3(d)–3(f) correspond to the products obtained at 1273 K for different times (d) 10.8 ks, (e) 18 ks, (f) 25.2 ks.
peaks in Fig. 3(b) can be indexed to ZrO\(_2\) (JCPDS card no. 78-1807) and ZrN (JCPDS card no. 89-3839), which indicated that a portion of ZrO\(_2\) has been converted to ZrN. The diffraction peaks in Fig. 3(c) can be indexed to Zr\(_3\)O and ZrN. The ZrO\(_2\) peaks disappeared, which indicates the ZrO\(_2\) has been converted to ZrN and a small amount of Zr\(_3\)O. In the possible reaction process could be illustrated as follows:

\[
\begin{align*}
2\text{NaN}_3 &\rightarrow 2\text{Na} + 3\text{N}_2 \\
3\text{ZrO}_2 + 5\text{Mg} &\rightarrow 5\text{MgO} + \text{Zr}_3\text{O} \\
\text{Zr}_3\text{O} + 2\text{Mg} &\rightarrow 2\text{MgO} + \text{Zr} \\
2\text{Zr} + \text{N}_2 &\rightarrow 2\text{ZrN} \\
2\text{Mg} + 2\text{Zr}_3\text{O} + 3\text{N}_2 &\rightarrow 2\text{MgO} + 6\text{ZrN}
\end{align*}
\]

The FE-SEM images of the products obtained at 1273 K for different times are shown in Figs. 3(d)–3(f). From the FE-SEM images, we find the products are composed of irregular particles. Only the product obtained at 1273 K for 3 h contains a small amount of nanoparticles, and the sizes of the products grow with the extension of the reaction time. In addition, all of the products obtained at 1273 K for 10.8–36 ks are zirconium nitride, the yield of the products increased with the extension of reaction time. The XRD patterns of the products obtained at 1273 K for 10.8 and 18 ks are shown in Fig. 4. In addition, the nitrogen content of the ZrN product was 13.02 %, slightly lower than the theoretical nitrogen content of zirconium nitride, possibly because the sample contained a small amount of oxygen.

By similar procedure, hafnium nitride (HfN) can also be obtained from the reaction of hafnium dioxide, sodium azide and metallic magnesium in an autoclave at 1273 K. XRD pattern of the as-prepared HfN product is shown in Fig. 5(a). All of the five diffraction peaks are found in the XRD pattern, which are almost the same position of the (111), (200), (220), (311), and (222) diffraction peaks of cubic phase HfN (JCPDS card no. 33-0592). In addition, the nitrogen content of the HfN product is 7.24 %, which is basically consistent with the theoretical nitrogen content of hafnium nitride. From the TEM image of the as-prepared HfN product [shown in Fig. 5(b)], the as-prepared HfN product is composed of particles. The size of the particles ranges from 50 to 200 nm. In our experiment, the preparation reaction of HfN used in our method can be expressed as:

\[
2\text{Mg} + \text{NaN}_3 + \text{HfO}_2 \rightarrow 2\text{MgO} + \text{HfN} + \text{Na} + \text{N}_2
\]

Compared with the traditional synthesis route, this synthesis method has several advantages. First, the reaction temperature of our preparation method is lower than that of the traditional method. On the other hand, the fabrication process is one-step synthetic reaction without expensive starting materials and apparatuses, which allows for the production of the ZrN and HfN powders on a large scale. In addition, our synthetic method can be developed as a universal method for the preparation of transition metal nitrides.

In this paper, ZrN powders have been successfully synthesized by utilizing zirconium dioxide, solid azide and metallic magnesium as starting materials in an autoclave. HfN powders can also be obtained from hafnium dioxide by the similar route.

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References

1) L. B. Wang, K. L. Zhang, H. L. Pan, L. Wang, D. Wang, W. C. Dai, H. F. Qin, G. R. Li and J. H. Zhang, *Nanoscale*, 10, 18936–18941 (2018).
2) M. B. Takeyama, T. Itoi, E. Aoyagi and A. Noya, *Appl. Surf. Sci.*, 190, 450–454 (2002).
3) L. B. Wang, K. B. Tang, Y. C. Zhu, Q. W. Li, B. C. Zhu, L. C. Wang, L. L. Si and Y. T. Qian, *J. Mater. Chem.*, 22, 14559–14564 (2012).
4) L. B. Wang, Q. W. Li, Y. C. Zhu and Y. T. Qian, *Int. J. Refract. Met. H.*, 31, 288–292 (2012).
5) L. B. Wang, W. J. Xian, K. L. Zhang, W. Q. Liu, H. F. Qin, Q. F. Zhou and Y. T. Qian, *Inorg. Chem. Front.*, 31, 288–292 (2012).
6) B. Tan, Y. Xiao, F. S. Galasso and S. L. Suib, *Chem. Mater.*, 6, 918–926 (1994).
7) E. G. Maksimov, S. Q. Wang, M. V. Magnitiskaya and S. V. Ebert, *Supercond. Sci. Tech.*, 22, 075004 (2009).
8) X. F. Ma, Z. Kang, X. Huang and G. J. Zhang, *J. Inorg. Mater.*, 30, 77–80 (2015).
9) S. Yugeswaran, P. V. Ananthapadmanabhan, L. Kumaresan, A. Kuberan, S. Sivakumar, G. Shanmugavelu and K. Ramachandran, *Ceram. Int.*, 44, 14789–14796 (2018).
10) J. Y. Li, Y. Sun, Y. Tan, F. M. Xu, X. L. Shi and N. Ren, *Chem. Eng. J.*, 144, 149–152 (2008).
11) E. G. Gillan and R. B. Kaner, *Inorg. Chem.*, 33, 1693–5700 (1994).
12) Y. Chen, C. J. Deng, C. Yu, J. Ding and H. G. Zhu, *Ceram. Int.*, 44, 8710–8715 (2018).
13) L. Yin and M. I. Jones, *Ceram. Int.*, 43, 3183–3189 (2017).
14) B. Mazumder, P. Chirico and A. L. Hector, *Inorg. Chem.*, 47, 9684–9690 (2008).
15) A. L. Hector, G. Henshaw, A. V. Komarov and I. P. Parkin, *J. Mater. Process. Tech.*, 77, 103–107 (1998).
16) X. M. Wu, G. H. Liu, J. Q. Li, Z. C. Yang and J. T. Li, *Ceram. Int.*, 44, 11914–11917 (2018).
17) R. A. Karaballi, G. Humagain, B. R. A. Fleischman and M. Dasog, *Angew. Chem. Int. Edit.*, 58, 3147–3150 (2019).
18) S. J. Zhao, J. T. Ma, R. Xu, X. P. Lin, X. Cheng, S. C. Hao, X. Y. Zhao, C. S. Deng and B. Liu, *Sci. Rep.*, 9, 19199 (2019).