Preparation of Nano-Scaled Nitride Powders by Direct Nitridation Method

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In this paper, a review on the synthesis of nanocrystalline nitride powders by direct nitridation of metal oxide nanoparticles, metal complex or salt in flowing ammonia gas is given. The nitrides include TiN, CrN, NbN, GaN, InN and BN. It is found that this method shows the great flexibility for preparing various kinds of nanocrystalline nitride powders with relatively simple production equipments, and is a promising route for mass production of nanocrystalline nitride powders. [Received August 4, 2003; Accepted December 18, 2003 ]

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1. Introduction

Metal nitrides have been intensively studied in the recent decades, and have found wide applications in modern industries, due to many of their peculiar properties. For example, TiN and CrN show very high hardness and excellent abrasion resistance, and are frequently used as wearing resistant coatings.1-3 Al2O3 and Si3N4 matrix composites reinforced with TiN show much improved mechanical properties and hardness, and are suitable candidates for cutting tool applications.4,5 InN and GaN are typical III-V semiconductors for application in optoelectronic devices such as light emitting diodes and laser diodes in the blue and ultraviolet range.6-8 NbN is well-known superconductor and has potential applications in superconductor devices, particularly in superconducting radiofrequency resonators as materials alternative to conventional metals (Pb, Nb).9 However, despite their great usefulness, there are great difficulties in synthesizing metal nitrides.

Metal nitrides are conventionally prepared by high temperature nitridation of metal, metal oxides, halides or hydrides in nitrogen, ammonia or nitrogen/hydrogen mixture gases, typically at temperature of around 1000°C over an elongated period. The problems associated with these processes include the huge energy consumption and the difficulty for obtaining nanosized powders, etc. Plasma-gas phase reaction, self-propagating high-temperature synthesis, high energy ball-milling and mechanically activated synthesis of metal nitrides are also reported.10-13 These methods either use complicated equipments, which are usually expensive, or the purities of the final products are low and needs further purifying treatments.

In the past two years, we developed a novel route for synthesizing of nanosized nitride powder by direct nitridation of metal oxide nanoparticles, metal complex or salt in flowing ammonia gas.14-19 This method shows the merits of the great flexibility for preparing various kinds of nanocrystalline nitride powders with relatively simple production equipments, and is a promising route for mass production of nanocrystalline nitride powders. In this paper, a brief review on this method is given.

2. Synthesis of Nitride Nanopowders by Direct Nitridation of Oxide Particles14-17

First, oxide nanopowders of TiO2, Cr2O3, Nb2O5 and In2O3 were prepared by chemical precipitation method using titanium butoxide, Cr(NO3)3·9H2O, Nb(OH)5 and In(NO3)3·4.5H2O as the starting materials, respectively. Then TiN, CrN, NbN and InN nanopowders were synthesized by direct nitridation of the oxide nanopowders in a tube furnace at different temperatures for various periods of time, using flowing ammonia gas as the nitriding agent.14-17

2.1 Effects of nitridation temperature on the formation of nitride powders

Figure 1(a) shows the XRD patterns of powders obtained by nitriding nanosized TiO2 at different temperatures for 5 hours.14 Distinct peaks assigned to titanium nitride appeared in the XRD pattern of the sample nitrided at 700°C, indicating that the cubic-phase TiN began to form at this temperature. However, the nitridation reaction was far from completion, because significant amounts of TiO2 and Ti2O3 still existed in this powder, as indicated by the strong TiO2 and Ti2O3 reflections. Phase pure TiN powder could only be obtained at 800°C and above.

Fig. 1 (b) shows the XRD patterns of samples obtained by nitriding Cr2O3 powder at 700°C-900°C for 8 h.15 The powder nitrided at 700°C was composed of CrN and residual Cr2O3,
while only CrN phase were detected in the samples nitrided at 800 and 900°C. As for NbN, Li found that pure NbN powder could be prepared by nitriding Nb2O5 nanopowder at 650°C for as long as 8 hours; however, when the nitriding temperature was increased to 700°C and above, the nitriding reaction completed in a shortening time of 3 hours.29

Therefore, it can be concluded that a high nitriding temperature was beneficial for the synthesis of high purity nitride powders, except for InN. Gao discovered that pure InN powder could only be obtained at a narrow temperature range of 580–620°C by direct nitriding In2O3 in ammonia gas.27 Below this temperature range, unreacted In2O3 remained in the final product; while above this temperature range, In metal droplets formed due to the decomposition of InN.

2.2 Effect of nitriding time on the formation of nitride powders

The nitriding time is another factor significantly influencing the synthesis of nitride powders. Keeping the nitriding temperature unchanged, the longer the nitriding time, the more complete the nitridation reaction. Figure 2(a) and (b) show the effects of nitriding time on the formation of TiN and CrN at 900°C and 800°C, respectively.14,15 Fig. 2(a) indicates that a powder mixture of rutile TiO2 and TiN was obtained when nitriding TiO2 at 900°C for 2 hours; whereas at the same nitriding temperature, no TiO2 was detected when the nitriding time was prolonged to 5 hours. In Fig. 2(b), the Cr2O3 was partially nitrided to CrN, when Cr2O3 was nitrided at 800°C for 4–6 h; whereas all Cr2O3 was converted to CrN when the nitriding time was prolonged to 8 h, despite that the nitriding temperature remained constant at 800°C. As to the case of NbN, it was found that considerable amount of residual Nb2O5 coexisted with NbN in the powder nitrided at 650°C for 5 hours, while the powder nitrided at 650°C for 8 hours composed of nearly pure NbN.16

The high sensitivity of nitridation reaction to the nitriding time implied that kinetic factors could have play important roles in controlling the reaction, which were likely the diffusions of N and or O atoms. This is due to that during the nitridation reaction, N and O atoms must diffuse through the nitride scale formed on the outside of oxide particle to facilitate the completion of the nitriding reaction.

2.3 Effect of nitriding temperature on the particle size of the nitride powder

The particle size of the nitride powder strongly depended on the nitriding temperature. Figure 3 shows the SEM images of TiN powders synthesized at 800–1100°C for 5 hours.34 The TiN particles in the powder synthesized at 800°C showed an average particle size of 20 nm. As the synthesizing temperature was raised to 900°C and 1100°C, the TiN particle size increased to 35 and 75 nm, respectively. The increase in the particle size of CrN and NbN with increasing nitriding temperature was observed in Fig. 4.15,16 Therein, the CrN particle size increased from 40–80 nm to 100–120 nm, as the nitriding temperature was increased from 800°C to 900°C; while the NbN particle size increased from 15–20 nm to 30–40 nm, as the nitriding temperature increased from 700°C and 800°C. Finally, it was observed for CrN and NbN powders, that the nitriding time also showed a significant influence on the nitride particle size.15,16 The longer the nitriding time, the larger the nitride particle size.

3. Synthesis of Nanocrystalline GaN Powder from Gallium(III)-Urea Complex18

The Gallium (III)-Urea complex was prepared as follows. First, 10.25 g of gallium (99.9999%) was dissolved in hydrochloric acid (36–38%), and was heated to be concentrated. After some ethanol was added, the solution was dried at 100°C to get a gelatin and then reacted with 52.98 g of urea (>99%) under stirring in ethanol. Ga(III)-urea complex was obtained after being dried at 110°C. An analysis of the IR spectrum of the complex indicated that only one nitrogen atom of each urea molecule coordinates to Ga3+ ion in the complex structure, the molecular formula was likely written as Ga(NH2CONH2)3Cl2. TG–DSC results indicated that the complex was not very stable, and the dissolution of the coordinated urea occurred at 150–350°C. GaN powders were prepared by nitridation of the complex powder at 500–900°C for 1 h in flowing ammonia. All the powders showed XRD patterns characterized to wurtzite GaN (Fig. 5).18 The XRD reflections became stronger and sharper with increase in the nitriding temperature, indicating a higher crystallization degree and a larger particle size of GaN. Figure 6 shows the TEM images of the GaN powders synthesized at 500 and 600°C.18 The particle sizes of both powders were on a nanometer scale, 13 nm for the sample synthesized at 500°C, and 24 nm for the sample synthesized at 600°C.

PL measurements of GaN powders were carried out using a fluorescence spectrometer with a Xe lamp (excited at 347 nm) at room temperature. All samples show a strong and narrow band-edge emission peak at 362 nm (Fig. 7).18 The powder synthesized at 500°C exhibited the strongest band-edge emission, together with a typical yellow luminescence at 400–620 nm and an impurity-related shoulder at 470 nm. The peak at 394 nm was not firmly identified. A dramatic decrease of the impurity-related emission and a minor decrease of the band-edge emission were observed as the nitriding temperature was increased. For the samples synthesized at 600 and 900°C, the yellow band was absent in their PL spectra. The present results show that a small particle size obtained at a lower temperature facilitates the band-edge emission, and 600°C should be an ap-
appropriate synthesis temperature for both a small particle size and good optical performance.

4. Synthesis of Nanosized BN Powder from \( \text{NH}_3\text{HBO}_2 \) Salt\(^{[9]} \)

First, a saturated \( \text{NH}_3\text{HBO}_2 \cdot 3\text{H}_2\text{O} \) aqueous solution was dripped into a \( \text{Ca}_3(\text{PO}_4)_2 \) ethanol alcohol suspension, then the \( \text{NH}_3\text{HBO}_2 \cdot \text{Ca}_3(\text{PO}_4)_2 \) precipitate was collected by filtration and dried at room temperature. The \( \text{NH}_3\text{HBO}_2 \) coated \( \text{Ca}_3(\text{PO}_4)_2 \) powder was nitrided at 900°C for 8 h to obtain a \( \text{Ca}_3(\text{PO}_4)_2-\text{BN} \) composite powder in the flow of \( \text{NH}_3 \) gas using a tube furnace. Nanosized BN powder was recovered from the \( \text{Ca}_3(\text{PO}_4)_2-\text{BN} \) composite powder after the later was treated with 6 M HCl solutions to dissolve the \( \text{Ca}_3(\text{PO}_4)_2 \) and washed with anhydrous ethanol for 3-5 times.

Figure 8 shows the IR spectrum of the as-prepared BN
powder. The strong peak at 1375 cm⁻¹ is assigned to the B-N stretching vibrations. The weak peak at 798 cm⁻¹ is attributed to B-N-B bending vibrations. No other peaks assigned to either NH₂HB₃O₃ or B₃O₃ were observed, which suggested that NH₂HB₃O₃ had been completely converted to BN after nitrided at 900°C for 8 h in NH₃.

Figure 9 shows the XRD patterns of the as-prepared BN powder and the BN powder obtained by crystallized the as-prepared BN powder at 1650°C for 2 h. Only distinct peaks assigned to h-BN appeared in the XRD patterns, and no other impurities were detected. This indicated that the BN nanopowders possessed high purity. The as-prepared BN powder was poorly crystallized as indicated by the broad XRD reflections, due to the high crystallizing temperature of h-BN (1600°C).

The crystallization temperature strongly affected the particle morphology of the BN powder. Fig. 10(a) shows the TEM image of the as-prepared BN powder. It consisted of BN nanofibers with a diameter of about 10 nm and a length of about 100-150 nm. After the as-prepared BN powder was crystallized at 1400°C for 2 h, the BN particles still remained the fibrous shape, as shown in Fig. 10(b). However, as the crystallization temperature was increased to 1650°C, the BN particle morphology changed dramatically. A number of rod-like BN particles with a diameter of about 25 nm and a length of about 100 nm formed, as shown in Fig. 10(c). Therefore, based on the above results, it can be concluded that BN powders with different particle morphologies can be prepared by varying the synthesizing conditions.

4. Summary

A review on the synthesis of nanocrystalline metal nitride powders by direct nitridation of metal oxide nanoparticles, metal complex or salt in flowing ammonia gas was conducted. It was found that the nitriding temperature and time were among the most important factors affecting the nitriding degree, the particle morphology and property of the final product. Various kinds of nanocrystalline nitride powders of high purity could be prepared by this method under controlled conditions, indicating the great flexibility of this method for

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**Fig. 5.** XRD patterns of GaN powders synthesized by nitriding Ga(III)-Urea complex at different temperatures for 1 hour.

**Fig. 6.** TEM images of GaN powders synthesized by nitriding Ga(III)-Urea complex at (a) 500°C and (b) 600°C for 1 hour.

**Fig. 7.** PL spectra of GaN powders synthesized at different temperatures.

**Fig. 8.** IR spectrum of BN powder nitrided at 900°C for 8 h.
the synthesis of nitride powders.

References

![Graph](image1)

**Fig. 9.** XRD patterns of BN powders (a) nitried at 900°C for 8 h and (b) crystallized at 1650°C for 2 h after nitridation at 900°C for 8 h.**

![Image 2](image2)

![Image 3](image3)

**Fig. 10.** TEM image of BN powders (a) nitried at 900°C for 8 h; (b) crystallized at 1400°C for 2 h after nitridation at 900°C for 8 h; (c) crystallized at 1650°C for 2 h after nitridation at 900°C for 8 h.**