Sulfur-assisted synthesis of nitride nanocrystals

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Received 30th September 2009, Accepted 1st December 2009 First published as an Advance Article on the web 5th February 2010 DOI: 10.1039/b920429f

A series of nitrides (TiN, ZrN, BN, AlN) were prepared by using the corresponding elements (Ti, Zr, B, Al), NaN₃ and sulfur as starting materials in a stainless steel autoclave at 250 °C. Sulfur was used to facilitate the exothermic reaction between NaN₃ and sulfur (at 250 °C) and the final formation of nitrides. The treatment temperature affected the growth of the nitride crystals, for example, diversified morphologies of TiN nanocrystals were formed in different temperature ranges: grain and truncated octahedron (250 °C), octahedron (>300 °C), and dendrite (>400 °C). Through similar processes, other nitrides (for example, TiN, AlN, Si₃N₄) could also be produced by employing NaNH₂ and additives (such as iodine or *N*-aminothiourea instead of sulfur) in low temperatures.

Introduction

Nitrides are important technological materials due to their properties including thermal, mechanical, and chemical stabilities, wide band-gap, or electrical conductivity.¹ Thus, nitrides can be applied in many fields, for example, as abrasion-resistant coatings and electroanalysis (TiN),² lubricants and optical coatings (BN),³ light- and field-emitting devices (AlN),⁴ superconducting films (ZrN),⁵ high-temperature ceramics and catalysts.⁶

Traditionally, nitrides have been synthesized by direct nitridation,⁷ carbothermal reduction and nitridation (> 1000 °C),⁸ self-propagating high-temperature synthesis (800–1300 °C),⁹ chemical vapor deposition (550-1500 °C),10 and ammonolysis of sulfides (> 750 °C).¹¹ Several general synthesis methods have also been developed. For example, the solid-state metathesis (SSM) route can be used to synthesize nitrides by using metal halides and Li₃N or NaN₃ (440-850 °C),¹² or by employing metal oxides with α -C₃N_{3.69},^{13a} or cyanamide/urea,^{13b} or Li₃N,^{13c} (600-1200 °C). Ammonolysis of organometallic precursors is applied to synthesize nitrides in relatively low temperatures: TiN $(150-450 \ ^{\circ}C)$,^{14a} ZrN (>300 $^{\circ}C)$,^{14b} AlN (>400 $^{\circ}C)$,^{14c} and BN (>800 °C).^{14d} Nitrides synthesized via this method often have a certain proportion of hydrogen content. Solvothermal synthesis is an effective method for the preparation of nitrides: TiN (350 °C),^{15a} ZrN (380 °C),^{15b} AlN (250 °C),^{15c} hexagonal and cubic BN (480 °C).15d However, it is still desired to develop general and simple methods to synthesize nitrides in lower temperatures.

Very recently, a sulfur-assisted approach was developed to synthesize Si_3N_4 nanocrystals (250 °C).¹⁶ In this study, a series of nitrides were prepared from the corresponding element powders *via* a sulfur-assisted synthesis process (SAS) following [eqn (1)]:

$$x\mathbf{M} + 2y\mathbf{NaN_3} + y\mathbf{S} \rightarrow \mathbf{M}_x\mathbf{N}_z + y\mathbf{Na_2S} + (6y - z)/2\mathbf{N_2} (\mathbf{M} = \text{Ti, B, Al, Zr})$$
(1)

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The whole reaction was started at 250 °C, TiN, BN, AlN, ZrN were formed at a treatment temperature of 250 °C. The possible reaction processes and the effect of treatment temperature on the shapes of the nitride crystals have also been discussed.

Experimental

Synthesis and purification

Ti powders (>99% purity, 200-300 mesh), B amorphous powders (>95.3% purity), Al powders (>99% purity, 100-200 mesh), Zr powders (>92% purity, 300 mesh), sublimed sulfur (>99.5% purity), NaN₃ (>98% purity). The amorphous B powders were purchased from Liaobin Chemical Co. Ltd. (Yingkou, China). All the other reagents used in the experiments were purchased from Shanghai Chemical Reagents Co.

In a typical synthesis procedure for TiN, Ti powder (0.01 mol), NaN₃ (0.042 mol), and sublimed sulfur (0.02 mol) were mixed and put into a 20 mL stainless-steel autoclave. Then the autoclave was sealed and heated from room temperature to 250 °C at a rate of 10 °C min⁻¹ and kept for 4 h. After it was naturally cooled to room temperature, the raw product was washed in turn with ethanol, distilled water, hydrochloric acid (0.5 M), distilled water and ethanol, finally dried in a vacuum oven at 60 °C for 8 h. By similar procedures, other nitrides (BN, AlN, ZrN) were synthesized starting from the corresponding elemental powders at 250 °C.

To study their effects on the morphology diversifications of the nitrides (TiN, BN, AlN, ZrN), different treatment temperatures (250–500 $^{\circ}$ C) were used. Details of the experiments and the morphologies of the nitrides products are listed in Table 1.

Characterization

The final products were characterized by an X-ray powder diffractometer (XRD; Bruker D8 with Cu-K α radiation), a scanning electron microscopy (SEM; JSM-6700F, 10 kV), a high-resolution transmission electron microscope (HRTEM; JEOL 2100; 200 kV) and X-ray photoelectron spectroscopy (XPS; VG ESCALAB 250 with monochromatized Al KR radiation).

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Starting metals, Molar ratio^a $T/^{\circ}C$, time/h Products, Space groups, JCPDS card No. Morphologies (most are in the nanometre scale) TiN, Fm3m, 38-1420 1 Ti, 1:2:4 250, >4grains, truncated octahedrons 2 300. > 0.2octahedrons, truncated octahedrons, grains 3 400, >0.2octahedrons, dendrites, truncated octahedrons, grains 4 250, >4 B, 1:4:8 BN, F63/mmc, 34-0421 membranes 5 ≥300, >2 membranes, quasi-hollow spheres 6 Al, 1:2:4 250. > 4AlN,F63/mc, 25-1133 particles 7 ≥300, >2 particles, short-rods, dendrites 8 Zr, 1:4:8 ZrN, Fm3m, 65-9411 250, >4grains grains, octahedrons ≥300, >0.5 " Refers to metal: sulfur: sodium azide

Table 1 Experimental conditions, structural information and morphologies of the as-obtained nitrides

Results and discussion

Fig. 1 shows the typical XRD patterns of the nitrides prepared *via* this sulfur-assisted synthesis (SAS): the raw product is a mixture of TiN (JCPDS #38-1420) and Na₂S (JCPDS #65-0525) before being washed (Fig. 1a); the following are patterns of pure nitrides: (b) TiN (JCPDS #38-1420), (c) BN (JCPDS #34-0421), (d) AIN (JCPDS #25-1133), (e) ZrN (JCPDS #65-7723). All the nitrides in Fig. 1 were obtained at 250 °C. The calculated cell parameters of these nitrides (listed in the caption of Fig. 1) are in agreement with their known values. In the contrast experiments, no significant peak shift was observed when the treatment temperature (250 °C) and time (4 h) were increased.



Fig. 1 Typical XRD patterns of the synthesized nitrides: (a) TiN before and (b) after being washed [the ● and ▼ indicate the diffraction peaks from TiN (JCPDS #38-1420, $a_1 = 4.243$ Å) and Na₂S (JCPDS #65-0525), respectively]; (c) ZrN (JCPDS #65-7723, $a_2 = 4.577$ Å); (d) AlN (JCPDS #25-1133, $a_3 = 3.108$ Å, $b_3 = 4.980$ Å); (e) BN (JCPDS #34-0421, $a_4 =$ 2.511 Å, $b_2 = 6.662$ Å). All the nitrides were obtained at 250 °C for 4 h.

The yields of TiN nanocrystals with different morphologies varied with the treatment temperature (Table 1; Fig. 2). TiN quasispherical nanograins and truncated octahedrons (with a diameter range of 50–150 nm) were the main products under a treatment temperature of 250 °C (Fig. 2a). TiN octahedra were formed above 300 °C, and the ratio of octahedra and truncated octahedra would reach ~80% at 400 °C (Fig. 2b). And TiN dendrites were found in the products above 400 °C, and its ratio would reach ~8% at 500 °C (Fig. 2c).

Undeveloped flat faces (Fig. 2a f1-f5) and edges (dashed lines) were found on some of the nanograins, which partly agreed with the nature of the truncated octahedron as reported previously.^{17a} High-magnification TEM images (inset) of the TiN nanograins show the distance of neighboring lattice fringes was 0.245 nm, corresponding to the (111) planes of TiN (JCPDS #38-1420). Compared to the nanograins, the octahedra are larger in diameter (100-300 nm) and have regular flat faces with clear edges (Fig. 2 b1). Also, some truncated or imperfect octahedra were formed, which might be as a result of the fast cooling rate during the reaction.^{17b,17c} The HRTEM image (Fig. 2 b2) taken from one corner of a TiN octahedron shows well defined 2D lattice planes and the distances of neighboring lattice fringes coincide with the (111) and (200) lattice spacings of TiN (JCPDS #38-1420). The corresponding fast Fourier transform (FFT) pattern (inset in Fig. 2b) can be assigned to face-centered cubic TiN, indicating that the octahedron is a single crystal with its [011] orientation parallel to the electron beam. Raising the treatment temperature would increase the yield of octahedral TiN nanocrystals.

TiN dendrites were observed in the as-synthesized products when the treatment temperature was increased above 400 °C. The TEM image (Fig. 2c) reveals the dendrites have hierarchical treelike branches, the SEM image (Fig. 2 d6) clearly shows the TiN three-dimensional (3D) dendritic structures: the secondary branches are parallel to each other in the same plane and perpendicular to the primary trunks. The lengths of the longest primary trunk and the secondary branches could reach 600 nm and 250 nm, respectively. The EDS spectrum (inset of Fig. 2c) indicates that the dendrites consist of Ti and N. Fig. 2d shows various TiN nanostructures obtained at 400 °C: grains (d1); octahedra (d2), overdeveloped octahedra (d3), undeveloped dendrites (d4), and developed dendrites (d5 and d6). It is thought that higher temperatures have more energy available to overcome activation barriers, and the product crystal growth will continue as long as the byproduct salt remains molten due to Ostwald ripening.¹⁸ Additionally, hotter reactions take longer to cool, more time will be available for crystal growth, generally leading to better crystallinity and greater yields.

The shape of nanocrystals is closely related to the crystallographic surfaces, because the crystal faces with higher growth rates will shrink and those with lower growth rates will expand during the crystal growth.^{17a} Low-index crystallography planes ({100} and {111}) are preferentially formed on the nanoparticle surface to lower the particle's surface energy. Thus, octahedra are the result



Fig. 2 (a) SEM images of TiN nanograins. Insets: a typical nanograin with undeveloped flat faces (f1–f4) and edges (dashed lines); a high-magnification TEM image taken from the top of a nanograin. (b) SEM images of TiN octahedra and truncated octahedra (b1); a HRTEM image taken from one corner of an octahedron (b2), inset: related fast Fourier transform pattern. (c) A typical TEM image of the TiN dendrites. Insets: a HRTEM image taken from the designated area (left) and the EDS spectrum (right). (d) SEM images with TiN nanostructures with different shapes: grain (d1); octahedron (d2); overdeveloped octahedron (d3); undeveloped dendrite (d4); developed dendrite (d5 and d6). The products were collected at 250 °C (a), 350 °C (b), and 400 °C (c) for 4 h, respectively.

of a high growth rate along the {100} faces,¹⁹ while dendritic or star-like structures are often formed through preferential growth of the [100] directions of truncated octahedra.²⁰ On the basis of the above theories, we could hypothesize the formation and the shape evolution of TiN nanocrystals as illustrated in Fig. 3. In the SAS, the system temperature was increased by the exothermic reaction of S/NaN₃ abruptly and decreased naturally to the heating temperature under a rapid cooling rate. TiN nuclei were formed from Ti powders and undergo a fast growth in all directions, which would produce quasi-spherical TiN nanograins. Because of the preferential growth of the $\{100\}$ facets, TiN nanocrystals undergo a shape evolution from grains to truncated octahedra, then octahedra, and finally dendrites.

Fig. 4 shows the XPS spectra of the TiN products obtained at 400 °C. The binding energy of N1s matches well with the literature value of 397.0 eV (upper-left in Fig. 4), and the binding energies



Fig. 3 A schematic of a proposed mechanism for the formation and shape evolution of TiN nanocrystals by SAS.



Fig. 4 XPS spectra of TiN nanocrystals synthesized at 400 °C for 4 h. Inset: N1s spectrum (upper-left); and Ti2p spectrum (upper-right).

of the Ti 2p doublet lines for TiN nanocrystals are 455.2 eV and 461.0 eV (upper-right in Fig. 4), which are in agreement with the published literature values for Ti2p3/2 and Ti2p1/2 spectra of titanium nitride, respectively.²¹ Quantitative analysis gives the average Ti:N atomic ratio of 1.05:1, this value is close to that of TiN. The appearance of carbon and oxygen signals in the survey spectrum (Fig. 4) might be attributed to surface oxidation or absorption.^{21b}

The transformations of B, Al and Zr powders to the corresponding BN, AlN and ZrN nanocrystals by SAS offer more examples to investigate the influence of the treatment temperature on the final shapes of the nitrides. BN membranes (Fig. 5a) with a thickness of ~2 nm are the dominating shape at 250 °C, while BN quasi-hollow spheres (Fig. 5b) were the main morphology above 400 °C. The honeycomb sp²-like bonded layers and a similar layered structure to graphite are the intrinsic reasons why membranous, tubular and vesicle-like BN could be synthesized.³ The typical morphologies of the obtained AlN were particles with a diameter of ~100 nm at 250 °C, and a few short-rods and dendrites could be formed at 400 °C (Fig. 5c). In the synthesis of ZrN, a low treatment temperature (250 °C) or a high Zr molar ratio of the reagents (Zr: S > 1:4) often results in the incomplete nitridation of Zr powders. ZrN particles with a diameter of 30 nm were the main products at 250 °C, while ZrN octahedra were formed above 400 °C (Fig. 5d). The EDS measurements and the HRTEM images (insets of Fig. 5c and 5d) indicated the AlN and ZrN nanocrystals are pure and well crystallized.

Chemical reactions of SAS

Previous works of SSM found that similar exothermic reactions often experience an intermediate state before product formation, which would change the original energy barrier (from precursor to product) into two smaller energy barriers: ΔE_{a1} (from precursor to intermediate) and ΔE_{a2} (from intermediate to product), then the entire reactions would occur in relatively low temperatures. (see Fig. 8 in Ref. 12c). Furthermore, the formation of thermodynamically favored by-products (such as H₂S, Li₂S, Na₂S, (NH₂)₂CS, *etc.*) assists the low-temperature synthesis of the nitrides.^{11,12e,15e}

Without the addition of sulfur, no binary nitride was formed from the reactions of the element powders and NaN₃ even at 600 °C. While the exothermic reaction between NaN₃ and S occurred at ~250 °C for 4 h from eqn (2).¹⁶ Then, the nitridation reactions were initiated. Taking Ti powders as an example, the energy released from the reaction between NaN₃ and S would support NaN₃ to decompose into Na and N₂, and release lots of energy [eqn (3)].²² All that energy released might support the transformation of Ti to TiS_x (0.5 $\leq x \leq$ 3) from eqn (4).²³ And TiN nanocrystals would be formed from a TiS_x/Na/N₂ mixture system [eqn (5)] similar to the SSM model.¹¹

$$\mathbf{S} + 2\mathbf{N}a\mathbf{N}_3 \to \mathbf{N}a_2\mathbf{S} + 3\mathbf{N}_2 \tag{2}$$



Fig. 5 TEM and related HRTEM images of nitride nanostructures: (a) BN membranes; (b) BN quasi-hollow spheres; (c) AlN particles and short rods; (d) ZrN particles and octahedra. Insets in c and d: SEM images and the corresponding EDS spectra. The products were collected at 250 $^{\circ}$ C (a) and 400 $^{\circ}$ C (b–d), respectively.

$$NaN_3 \rightarrow 2Na + 3N_2 \tag{3}$$

$$Ti + xS \rightarrow TiS_x$$
 (4)

$$TiS_x + 2xNa + 1/2N_2 \rightarrow xNa_2S + TiN$$
(5)

Meanwhile, another possible reaction pathway might have occurred. The reaction between NaN_3 and sulfur will produce a large amount of heat energy [eqn (2)], which might support the direct transformation from Ti to TiN through a progress similar to the SHS model:¹⁰

$$Ti + 1/2N_2 \rightarrow TiN$$
 (6)

However, both equations of these reaction models can be expressed as:

$$\mathrm{Ti} + 4\mathrm{NaN}_3 + 2\mathrm{S} \to \mathrm{TiN} + 2\mathrm{Na}_2\mathrm{S} + 11/2\mathrm{N}_2 \tag{7}$$

The calculated thermodynamic factor values can also support the above assumption:²⁴ reactions [eqn (2)–eqn (7)] are thermodynamically spontaneous (*e.g.* $\Delta G^{\circ}(6) = -287.3$ kJ mol⁻¹, $\Delta G^{\circ}(7) =$ -1467.2 kJ mol⁻¹) and exothermic (*e.g.* $\Delta H^{\circ}(6) = -338.4$ kJ mol⁻¹, $\Delta H^{\circ}(7) = -1165.6$ kJ mol⁻¹). Because $\Delta G^{\circ}(7) \ll \Delta G^{\circ}(6) < 0$, and $\Delta H^{\circ}(7) \ll \Delta H^{\circ}(6) < 0$, the reaction in eqn (7) (SAS) is more prone to occur than that in eqn (6) (SHS).

In this SAS process, TiN could not be obtained if the treatment time was shorter than 4 h at 250 °C, while TiN could be formed within 10 min when the treatment temperature was increased above 300 °C. Other nitrides (BN, AIN, ZrN) could also be obtained through SAS at 250 °C. While elements like vanadium(v), chromium (Cr) and tungsten (W) need higher temperatures (VN: 400 °C; CrN: 450 °C; WN: 450 °C) to be converted into related nitrides by a similar method; metals like Cr and W are often used as additives to enhance the corrosion resistance and mechanical strength of low-alloy steels.²⁵ The average yields (calculated according to the amount of elements) of each product are: 52% (TiN), 41% (BN), 44% (AIN), 45% (ZrN), 37% (VN), 32% (CrN), 30% (WN).

Up to now, SHS (or combustion synthesis) has been successfully applied to prepare lots of nitrides (e.g. Si₃N₄, TiN, AlN, etc.),⁹ however, to the best of our knowledge, GaN/InN has not been synthesized through an SHS method (or combustion synthesis) by using metallic Ga/In as the gallium or indium source. Our experimental results are consistent with them to some extent: no TiN/AlN has been obtained by using Ti/Al ribbons (1 cm long, 0.5 cm wide, and 0.2 mm thick) instead of Ti/Al powders (~200 mesh); Neither GaN nor InN has been obtained from metallic Ga/In by this method. As the melting points of Ga (29.89 °C) and In (156.40 °C) are lower than 250 °C, but the boiling points of Ga (2203 °C) and In (2072 °C) are markedly higher than 250 °C. Thereby, the Ga and In would melt into liquids and congregate at 250 °C. And we found only Ga/In bulk solids but not GaN/InN nanocrystals in the final products. According to previous reports, crystals with a smaller size would have a higher specific surface area along with a higher specific surface energy,²⁶ which would result in some different physical properties and chemical reactivities in contrast to the bulk materials.²⁷ It is considered that the preferential formation of Ga/In bulk molten liquids (at 250 °C) with low specific surface area, low specific surface energy and low chemical reactivities might be the major reason why GaN/InN could not be formed by this method. However, the exact reasons still need further investigation.

 $NaN_3/NaNH_2 + additives \rightarrow N_2/NH_3/H_2 + by-products$ (8)

$$M + NaN_3/NaNH_2 + additives \rightarrow MN + N_2/NH_3/H_2 + by-products (additive = S, I_2, N-aminothiourea) (9)$$

It was found that other additives such as iodine (I_2) or N-aminothiourea could also react acutely with NaN₃ or NaNH₂ at relatively low temperature, and some thermodynamically favored by-products (Na₂S, NaI) would form [eqn (8)]. If iodine or Naminothiourea was used instead of sulfur in the SAS process similar to the synthesis of Si₃N₄,²⁸ nitrides (TiN, AlN) could also be obtained under a treatment temperature below 200 °C. When NaN₃ was substituted by NaNH₂ in the SAS process, nitrides (TiN, AlN, Si₃N₄) could also be synthesized at 380 °C (above the decomposition temperature of NaNH₂).²⁹ Presently, this general additive-assisted method [eqn (9)] has successfully been applied to synthesize eight nitrides (TiN, AlN, BN, ZrN, Si₃N₄, VN, CrN, WN). The exact reaction mechanism requires further investigation. More chemicals will be investigated to replace sulfur or NaN₃ in preparing nitrides by similar additive-assisted methods. [Caution: the reaction between $NaNH_2$ and I_2 can occur below 100 °C, and I_2 can react intensively with extra Na (decomposed from NaN_3 or $NaNH_2$ during the purification of the raw products.]

Conclusions

The SAS process offers a general and simple method for the synthesis of nitrides (TiN, AlN, BN, ZrN, Si_3N_4 , VN, CrN, WN) from element powders. The exothermic reaction between NaN₃ and S was favorable for the final formation of nitrides at relatively low temperature. Nitride nanocrystals with regular shapes could be formed at higher treatment temperatures (>400 °C). Instead of sulfur and NaN₃, other additives (I₂ or *N*-aminothiourea) and NaNH₂ were successfully used to synthesize several nitrides (TiN, AlN, Si₃N₄) at extremely low temperatures.

Acknowledgements

This work was financially supported by the National Natural Science Found of China (Nos. 20871075, 20971079), the Ph.D. Programs Foundation of Ministry of Education of China (No. 20070422046), and the 973 Project of China (No. 2005CB623601), and Independent Innovation Foundation of Shandong University.

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