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Low Temperature Induced Synthesis of TiN Nanocrystals

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TiN nanocrystals were successfully prepared through the direct reaction between $TiCl_4$ and $NaNH_2$ induced at 300 °C. The yield based on Ti is approximately 80%. X-ray powder diffraction indicated that the product was cubic TiN with a lattice constant of $a = 4.243$ Å. Transmission electron microscopy revealed that nanocrystalline TiN with a diameter of 10 nm or so and extremely long straight rods were synthesized. The possible formation mechanism was also proposed.

Titanium nitride (TiN) attracts considerable technological interest because of its high melting point (2950 °C), superior high-temperature strength, high chemical and thermal stability, excellent corrosion and wear resistance, good thermal and electrical conductivity, and gold color.[1−3] These attractive properties enable it to be used as diffusion barriers in microelectronics,[4] as hard, protective coatings for cutting tools,[5,6] and as crucibles in metal smelting. Nanocrystalline TiN may find promising applications in mechanical, tribological, and high-performance ceramic fields.[7]

Generally, TiN was prepared via the reaction of metal titanium with nitrogen or ammonia at temperatures above 800 °C[2,8] or nanosized titania nitrified in flowing ammonia gas at 700−1100 °C.[9,10] An alternate method was mechanical milling, wherein the reactant was ground for extended periods of time and subsequently heated in a nitrogen atmosphere.[11,12] A hydrazide sol−gel process was adopted to prepare crystalline TiN at temperatures above 800 °C in ultrahigh purity (UHP) nitrogen and UHP Ar atmospheres.[13] Self-propagation high-temperature synthesis was reported to form TiN by heating or igniting fine titanium powders under high nitrogen pressures, but the reaction was often incomplete.[14,15] Solid-state metathesis was a route to rapidly prepare TiN by the reaction between $TiCl_3$ and sodium azide or lithium nitride.[16,17] Solvothermal synthesis was another method to synthesize TiN nanocrystals at 350−380 °C using $TiCl_4$ and sodium azide as source materials, but amorphous carbon from the carbonization of benzene is inevitable.[18] Chemical vapor deposition (CVD)[19−23] has also been developed to synthesize TiN.

Herein, we describe a direct and convenient route to prepare TiN nanocrystals at 300 °C via the reaction of $TiCl_4$ with $NaNH_2$. Though a similar reaction between $TaCl_5$ and $LiNH_2$ or $LiNMe_2$ was used to synthesize TaN and Ta_3N_5,[24] to the best of our knowledge, it is the first time to prepare nanocrystalline TiN with $NaNH_2$ as nitrogen source. The

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(1) Shaffer, P. T. *Plenum Press Handbook of High-Temperature Materials*; Plenum Press: New York, 1964; Vol. 1, pp 262−294.
(2) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic Press: New York, 1971.
(3) Lengauer, W. *Surf. Interface Anal*. **1990**, *15*, 377.
(4) Östling, M.; Nygren, S.; Petersson, C. S.; Norström, H.; Buchta, R.; Blom, H. O.; Berg, S. *Thin Solid Films* **1986**, *145*, 81.
(5) Maatsumura, Y.; Chujo, T.; Uchida, H.; Uchida, H. H. *Surf. Coat. Technol*. **1993**, *60*, 489.
(6) Buhl, R.; Pulker, H. K.; Moll, E. *Thin Solid Films* **1981**, *80*, 265.
(7) Andrievski, R. A. *Nanostruct. Mater*. **1997**, *9*, 607.
(8) Blumenthal, W. B. *The Chemical Behavior of Zirconium*; Van Nostrand: Princeton, NJ, 1958.
(9) Kawano, S.; Takahashi, J.; Shimada, S. *J. Am. Ceram. Soc*. **2003**, *86*, 1609.
(10) Li, J. G.; Gao, L.; Zhang, Q. H.; Sun, J.; Li, W. *J. Inorg. Mater*. **2003**, *18*, 765.
(11) Eleskandarany, M. S.; Sumiyama, K.; Aoki, K.; Suzuki, K. *J. Mater. Res.* **1992**, *7*, 888.
(12) Ren, R. M.; Yang, Z. G.; Shaw, L. L. *Mater. Sci. Eng. A* **2000**, *286*, 65.
(13) Kim I. S.; Kumta, P. N. *J. Mater. Chem.* **2003**, *13*, 2028.
(14) Munir, Z. A. *Am. Ceram. Soc. Bull.* **1988**, *67*, 342.
(15) Holt, J. B. (U.S. Department of Energy). Refractory Materials. U.S. Patent 4,459,363, July 10, 1984.
(16) Gillan E. G.; Kaner, R. B. *Inorg. Chem.* **1994**, *33*, 5693.
(17) Janes, R. A.; Aldissi, M.; Kaner, R. B. *Chem. Mater*. **2003**, *15*, 4431.
(18) Hu, J. Q.; Lu, Q. Y.; Tang, K. B.; Yu, S. H.; Qian, Y. T.; Zhou, G. E.; Liu, X. M. *J. Am. Ceram. Soc.* **2000**, *83*, 430.
(19) Ianno, N. J.; Ahmed, A. U.; Englebert, D. E. *J. Electrochem. Soc.* **1989**, *136*, 276.
(20) Kato, A.; Tamari, N. *J. Cryst. Growth* **1995**, *29*, 55.
(21) Yun, J. Y.; Rhee, S. W. *Thin Solid Films* **1998**, *312*, 24.
(22) Wang, S. T.; Zhang, Z. *Prog. Chem.* **2003**, *15*, 374.
(23) Tsao, C. J.; Du, Y. S.; Miao, H. F. *J. Electrochem. Soc.* **1987**, *134*, 476.
(24) Parkin, I. P.; Rowley, A. T. *Adv. Mater*. **1994**, *6*, 780.

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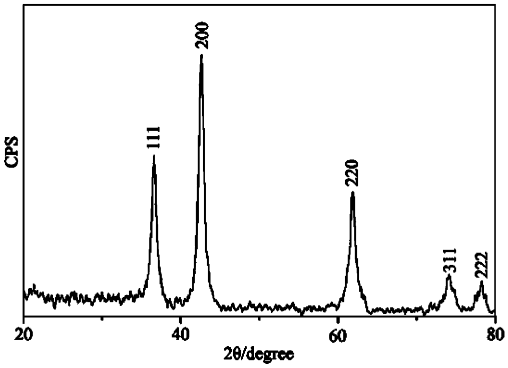

Figure 1. XRD pattern of TiN nanocrystals.

crystals were characterized by X-ray powder diffraction and transmission electron microscopy.

The starting materials used in this work were analytical pure grade anhydrous $TiCl_4$ and $NaNH_2$. In a typical procedure, 6 mL of $TiCl_4$ and 5 g of $NaNH_2$ were put into a stainless steel autoclave of 50 mL capacity. All the manipulations were carried out in a protecting N_2 gas flow. After the autoclave was sealed, it was heated to 300 °C, held for 10 h at that temperature, and then allowed to cool to ambient temperature in the furnace. The product was collected, filtered, and washed with absolute ethanol, hot hydrochloric acid, and distilled water successively to remove unreacted reagent, byproduct of NaCl, and other impurities. After being dried fully in a vacuum at 60 °C, 1.6 g of black powder was ultimately obtained.

X-ray powder diffraction (XRD) was performed on a Rigaku D max-γA X-ray diffractometer with Ni filtered Cu Kα radiation ($V = 50$ kV, $I = 100$ mA) at a scanning rate of 4°/min. The morphology of TiN nanocrystals was examined using a Hitachi H-800 transmission electron microscope (TEM) at an accelerating voltage of 150 kV.

Figure 1 shows the XRD pattern of the sample; all of the peaks can be indexed to cubic TiN (belonging to the $Fm\bar{3}m$ space group) with a lattice constant of $a = 4.243$ Å, which is in good agreement with the JCPDS card No. 38-1420. No impurities were detected. The broadening nature of the peaks indicates that the sample is composed of nanocrystallites. The average size of the product is about 10 nm calculated by the Debye−Scherrer equation.[25]

Figure 2 is the typical TEM morphology of the TiN nanocrystals and the corresponding electron diffraction pattern (EDP). It can be seen that the crystals consist mainly of spherical particles with an average size of 10 nm or so, which is in good agreement with the result from the XRD pattern. From the EDP, the d values corresponding to the diffraction rings (from the inner to the outer) are 2.4496, 2.1214, 1.5008, and 1.2789 Å, which can be assigned to the planes of (111), (200), (220), and (311) of the cubic TiN, respectively. Extremely long straight rods, with a yield of 15% or so, can be easily observed in the sample. Figure 3 shows one of these rods and the corresponding EDP. The diameter of the rod is about 175 nm, and the length is near 25 μm. From the EDP, the growth direction of the rod is perpendicular to the (111) plane.

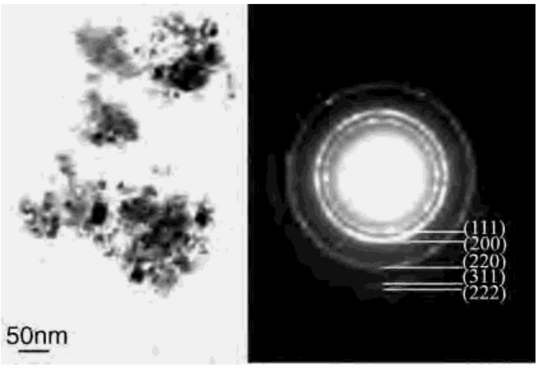

Figure 2. TEM morphology of nanocrystalline TiN and the corresponding diffraction pattern.

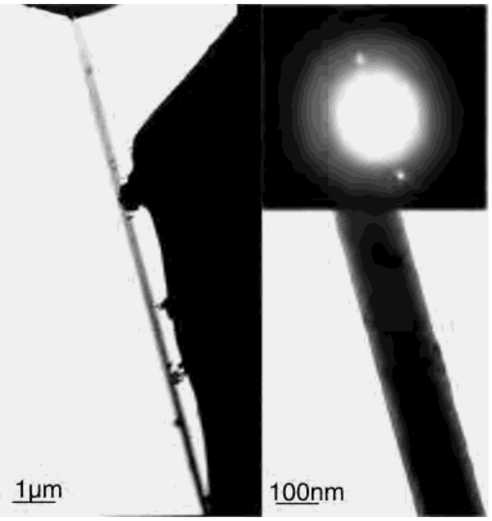

Figure 3. TEM morphology of TiN rod and the corresponding diffraction pattern.

The possible formation mechanism of TiN nanocrystals was proposed as follows. With raising the temperature to 300 °C, $TiCl_4$ vaporized (boiling point: 136.4 °C) and $NaNH_2$ melted (melting point: 208 °C); a gas−liquid interface, as a result, was provided. However, the temperature in our experiment is much lower than the decomposition temperature of $NaNH_2$ (above 500 °C).[26] This demonstrates that $TiCl_4$ and $NaNH_2$ may react directly without the need of decomposing $NaNH_2$. The possible reactions may be divided into the following two steps:

$$TiCl_4 + 4NaNH_2 = Ti(NH_2)_4 + 4NaCl \qquad (1)$$

$$6Ti(NH_2)_4 = 6TiN + 16NH_3 + N_2 \qquad (2)$$

These two reactions may be combined into one:

$$6TiCl_4 + 24NaNH_2 = 6TiN + 24NaCl + 16NH_3 + N_2 \qquad (3)$$

To our knowledge, the thermodynamic properties of $Ti(NH_2)_4$ are not available in the literature. So we merely calculated the free energy and enthalpy of reaction 3, which

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(25) Analysis Center (Ed.) *XRD Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985.

(26) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999.

is thermodynamically spontaneous ($\Delta G_f^\circ = -830.73$ kJ/mol) and highly exothermic ($\Delta H_f^\circ = -733.31$ kJ/mol), which can be verified by the fact that the maximum temperature outside the autoclave reached 352 °C (52 °C higher than the temperature designed) after heating for 50 min from ambient temperature. However, the reaction cannot take place when the temperature is lower than the melting point of $NaNH_2$. Once reaction 1 starts, it gives out heat energy rapidly and initiates reaction 2 almost at the same time. Thus results in a transient high temperature and the molten byproduct of NaCl (melting point: 800.8 °C), which is favorable to the formation and crystallization of TiN. Nevertheless, the heat energy produced during the reactions was transferred rapidly to the autoclave and released. Therefore it is not long enough for ultrafine TiN to grow into a large size, and thus was obtained nanocrystalline TiN. Here NaCl may also play an additional significant role in avoiding the agglomeration of the TiN crystals.

In summary, TiN nanocrystals were successfully prepared by the direct reaction between $TiCl_4$ and $NaNH_2$ induced at low temperature (300 °C) in autoclave. The average size of the particles is about 10 nm. Moreover, a lot of straight long TiN rods were also synthesized.

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