Chem. Mater. **2003,** *15,* 4431−4435

Controlling Surface Area of Titanium Nitride Using Metathesis Reactions

Rebecca A. Janes,[†] Matt Aldissi,[‡] and Richard B. Kaner*[,†]

Department of Chemistry and Biochemistry, and Exotic Materials Institute,
University of California, Los Angeles, Los Angeles, California 90095-1569, and
Fractal Systems, Inc., 200 9th Avenue North, Safety Harbor, Florida 34695

Received July 14, 2003

A metathesis (exchange) reaction between $TiCl_3$ and Ca_3N_2 produces phase-pure titanium nitride, TiN, after washing away the $CaCl_2$ byproduct salt. With use of in situ thermocouples, a maximum reaction temperature (T_{max}) of 1665 °C is measured for a reaction producing 1.0 g of TiN 0.6 s after initiating the reaction with a resistively heated Nichrome filament. Scanning electron microscopy indicates the formation of micrometer-size TiN particles. Reduction of the reaction size and addition of 3 mol of NH_4Cl lowers the reaction temperature to 965 °C and decreases the time the $CaCl_2$ byproduct remains in a molten state from 9 to 0.6 s. This suppresses Ostwald ripening of the TiN, decreasing the crystallite size and increasing its surface area. Line broadening of X-ray diffraction peaks shows a decrease in the average crystallite size from >200 to 30.8 nm, consistent with 20−30-nm-size particles observed using transmission electron microscopy. Nitrogen gas absorption (BET) indicates that the surface area of the TiN increases from 16.0 to 71.3 m^2/g. Higher surface area TiN can be used to improve the performance of electrodes in supercapacitors. Experiments with 26 m^2/g TiN result in a capacitance of >100 F/g and a Coulombic efficiency near 100% even after 10^6 cycles of charging and discharging.

Introduction

Titanium nitride (TiN) is a useful material because of its many superior properties including wear resistance, hardness (2160 kg/mm^2), oxidative stability, corrosion resistance, and high conductivity (5×10^4 $\Omega^{1-}cm^{-1}$).[1,2] These latter three qualities make TiN an excellent candidate for electrodes in electrochemical capacitors, which use highly corrosive electrolytes such as potassium hydroxide. Currently bulk TiN powders are generally produced through reaction of the metal with nitrogen or ammonia at high temperatures.[3,4] This process is time-consuming since additional heating may be required to fully nitride any lower nitrides or unreacted metal in the product.[5,6] Other synthetic routes to TiN include high-energy mechanical milling, in which the titania reactant is ground for at least 48 h and subsequently heated in a nitrogen atmosphere,[7] laser-assisted CVD to produce films from $TiCl_4$ and N_2,[8] and light ion beam evaporation, in which fine TiN powders are produced from a Ti target in a N_2 atmosphere.[9] Another route to nitrides known as self-propagating high-temperature synthesis (SHS) uses finely divided metal powders heated in the presence of high nitrogen pressures or sodium azide as a solid nitrogen source.[10−12] These high-temperature techniques generally lead to materials with low surface areas, and therefore may not be the best approach for electrode materials.

Another synthetic technique that can produce materials rapidly and offers control over reaction temperatures is known as solid-state metathesis (SSM) reactions. These exothermic reactions are driven by the formation of thermodynamically stable salt byproducts, which are easily washed away with water or methanol after reaction completion. Initiation of these self-propagating reactions can be achieved through the use of a heated filament. Upon initiation of the precursor salts, high temperatures (often >1400 °C) are very rapidly (often < 1 s) generated and then quickly dissipated. This generally results in a relatively high yield of crystalline product.[13] Metathesis reactions have proven to be successful in the synthesis of a number of refractory materials including borides,[14] chalcogenides,[15,16] and

---

* To whom correspondence should be addressed. kaner@chem.ucla.edu
[†] University of California, Los Angeles.
[‡] Fractal Systems, Inc.

(1) Pierson, H. O. *Handbook of refractory carbides and nitrides: properties, characteristics, processing, and applications*; Noyes Publications: Park Ridge, NJ, 1996.

(2) Shackelford, J. F.; Alexander, W. *CRCnetBASE (Online service) CRC materials science and engineering handbook*, 3rd ed.; CRC Press: Boca Raton, FL, 2001.

(3) Toth, L. E. *Transition metal carbides and nitrides*; Academic Press: New York, 1971.

(4) Blumenthal, W. B. *The chemical behavior of zirconium*; Van Nostrand: Princeton, NJ, 1958.

(5) Eslamloogrami, M.; Munir, Z. A. *J. Am. Ceram. Soc.* **1990**, *73*, 2222−2227.

(6) Deevi, S.; Munir, Z. A. *J. Mater. Res.* **1990**, *5*, 2177−2183.

(7) Ren, R. M.; Yang, Z. G.; Shaw, L. L. *Mater. Sci. Eng., A* **2000**, *286*, 65−71.

(8) Ishihara, S.; Hanabusa, M. *J. Appl. Phys.* **1998**, *84*, 596−599.

(9) Nakagawa, Y.; Grigoriu, C.; Masugata, K.; Jiang, W. H.; Yatsui, K. *J. Mater. Sci.* **1998**, *33*, 529−533.

(10) Munir, Z. A.; Holt, J. B. *J. Mater. Sci.* **1987**, *22*, 710−714.

(11) Holt, J. B. U.S. Department of Energy, U.S. Patent 4459363, 1984.

(12) Holt, J. B. U.S. Department of Energy, U.S. Patent 4459363, 1984.

(13) Gillan, E. G.; Kaner, R. B. *Chem. Mater.* **1996**, *8*, 333−343.

10.1021/cm034629n CCC: $25.00

nitrides.[14,17,18] Since the reaction temperature and therefore the time for nucleation and growth of crystallites can, in principle, be controlled, high surface area products are possible but have not until now been explored.

Here, control over surface area is demonstrated for titanium nitride. Phase-pure TiN is synthesized in seconds from a metathesis reaction between Ca_3N_2 and $TiCl_3$. Addition of different molar ratios of salt to the reactants lowers the reaction temperature, thereby shortening the nucleation and growth time for the crystallites, and produces relatively high surface area materials. This could prove useful for applications requiring high surface area such as electrodes for supercapacitors. Here, the titanium nitride product is characterized using powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, in situ temperature analysis, thermogravimetric analysis, and electrochemical capacitance.

Experimental Section

The reagents, $TiCl_3$ (Strem, 98+%, Al-reduced), $TiCl_3$ (Aldrich, 99%, H_2-reduced), TiI_4 (Gelest, 99.9%), Li_3N (Cerac, 99.5%), Ca_3N_2 (Cerac, 99%), NaN_3 (Strem, 98%), NH_4Cl (Cerac, 99.999%), $CaCl_2$ (Aldrich, tech), LiCl (Fischer, 99.5%), $NaNH_2$ (Alfa Aesar, 96%), $LiNH_2$ (Alfa Aesar, 95%), and TiN (Powdermet; Nanotechnology; Cerac, 99.5%), were all used as received.

The synthesis of titanium nitride is carried out in a helium-filled glovebox (Vacuum Atmospheres MO-40). The amount of reactants is adjusted to produce 0.25 g (4.0 mmol), 0.5 g (8.1 mmol), or 1.0 g (16.2 mmol) of TiN product. Stoichiometric amounts of the reactants are weighed and ground together with an agate mortar and pestle. The reactants are then transferred to a stainless steel cup and placed within a larger capped steel reaction vessel, modeled after a bomb calorimeter.[19] This allows for containment of any gases produced. A resistively heated Nichrome wire is used to initiate the reaction, which is complete in less than a second. Warning: *Solid-state metathesis reactions are highly exothermic, and may initiate upon grinding reagents together. Precautions should be taken before performing this type of reaction and extreme care used when scaling up reactions*. The reaction products are then removed from the drybox and washed in water followed by either vacuum filtration or centrifugation (Beckman J2-HS) with final drying under vacuum.

In situ reaction temperature measurements are made through a modification of the stainless steel reactor vessel. A hole is drilled through the bottom of both the steel canister and the reaction cup. A high-temperature thermocouple—0.03-in. diameter C-type (Omega, 26% rhenium/84% tungsten versus 5% rhenium/85% tungsten)—is threaded through the hole and placed directly into the reaction mix and secured with ceramic paste. A computer is connected to the thermocouple and records one data point every millisecond.

The capacitance of titanium nitride with a surface area of 24 m^2/g was tested by using it as both the anode and the cathode in a capacitance cell. The electrodes are separated by an electrically insulating 25-μm porous polypropylene/polyethylene film (Celgard #3400). The electrodes are prepared by soaking them in an electrolyte of concentrated potassium hydroxide for 72 h. The wet electrodes and separator material are then placed into a silicone gasket supported by stainless steel disks on each side to form a $^1/_2$-in. diameter, 0.1-mm thick cell assembly that is sealed for carrying out electrochemical tests.

Product Characterization

Powder X-ray diffraction is performed on the washed products using a Crystal Logic $\theta-2\theta$ diffractometer with a graphite monochromator and Cu Kα = 1.5418 Å radiation. The scans were taken between 10° and 100° 2θ at 0.1° intervals with a 3-s count time. Least-squares refinement is carried out using MacDiff (http://www.geol.uni-erlangen.de/html/software/Macdiff.html) to fit the X-ray diffraction peaks and Unit Cell (http://www.esc.cam.ac.uk/astaff/holland/UnitCell.html) to calculate the lattice parameters. Scanning electron microscopy (SEM-Stereoscan 250) is used to characterize surface structure and particle size of the product. Transmission electron microscopy (TEM JEOL 100CX) is used to determine the size of the crystallites. Thermogravimetric analysis (Perkin-Elmer Pyris Diamond TG/DTA) is carried out from room temperature to 1500 °C, at a rate of 10 °C/min, and hydrogen-reduced $TiCl_3$ is used to synthesize the TiN for the TGA analysis. Brunauer−Emmet−Teller (BET) surface area analysis is performed using nitrogen gas absorption (Micromeritics 2010).

Results and Discussion

TiN is a desirable material because of its many favorable physical attributes, ranging from high conductivity and hardness to resistance to chemical attack. These properties make TiN useful for a variety of applications, including as an electrode in supercapacitors. A capacitor consists of two metal electrodes separated by an electrically insulating (dielectric) medium. Capacitance (C) of a material is governed by $C = \epsilon_0 A/d$, where ϵ_0 is the permittivity of vacuum, A is the cross-sectional area of the electrode plates, and d is the distance between plates. To improve the capacitance for a dielectric with a given separation between electrodes, the area of the plates must be increased. Although this is traditionally accomplished by increasing the size of the plates, an alternative is to increase the surface area of the electrode material. This approach is explored here by varying the synthetic conditions used to produce TiN.

To make higher surface area materials in a metathesis reaction, the length of time in which the product spends within a molten salt matrix is critical. The less time spent in the molten salt, the less Ostwald ripening will occur, resulting in smaller crystallites with higher surface area. Previous metathesis experiments have shown that the use of salts as diluents lowers the maximum reaction temperature (T_{max}).[17,20−22] If T_{max} is lower, it follows that the amount of time the products remain above the melting point of the byproduct salt will be reduced. To explore this idea, several diluents were tested, including LiCl, $CaCl_2$, NaN_3, $NaNH_2$, $LiNH_2$, and NH_4Cl.

One difficulty experienced with diluents is maintaining phase homogeneity in the TiN product. This includes incomplete nitridation, resulting in subnitride formation

---

(14) Rao, L.; Gillan, E. G.; Kaner, R. B. *J. Mater. Res.* **1995**, *10*, 353−361.

(15) Gillan, E. G.; Kaner, R. B. *J. Mater. Chem.* **2001**, *11*, 1951−1956.

(16) Hector, A.; Parkin, I. P. *Polyhedron* **1993**, *12*, 1855−1862.

(17) Wallace, C. H.; Reynolds, T. K.; Kaner, R. B. *Chem. Mater.* **1999**, *11*, 2299−2301.

(18) Fitzmaurice, J. C.; Hector, A.; Parkin, I. P. *Polyhedron* **1993**, *12*, 1295−1300.

(19) Bonneau, P. R.; Wiley, J. B.; Kaner, R. B. *Inorg. Synth.* **1995**, *30*, 33−37.

(20) Cumberland, R. W.; Blair, R. G.; Wallace, C. H.; Reynolds, T. K.; Kaner, R. B. *J. Phys. Chem. B* **2001**, *105*, 11922−11927.

(21) Janes, R. A.; Low, M. A.; Kaner, R. B. *Inorg. Chem.* **2003**, *42*, 2714−2719.

(22) Aguas, M. D.; Nartowski, A. M.; Parkin, I. P.; Mackenzie, M.; Craven, A. J. *J. Mater. Chem.* **1998**, *8*, 1875−1880.

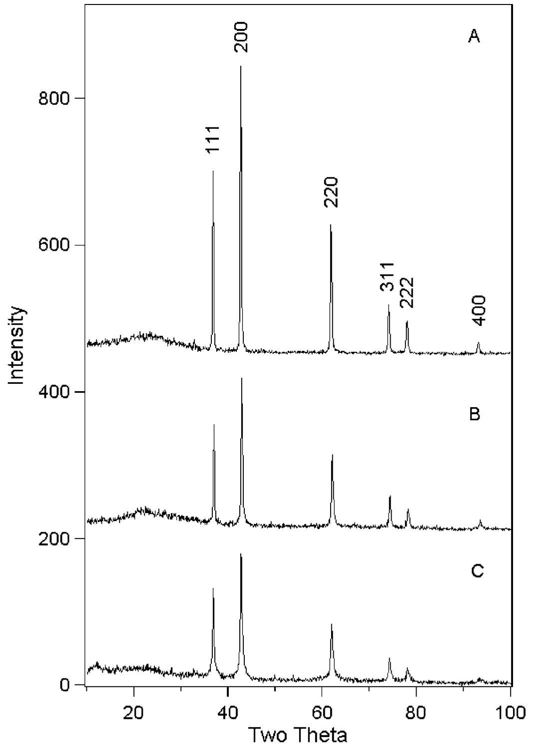

Figure 1. Powder X-ray diffraction patterns of TiN produced by metathesis reactions between $2TiCl_3 + Ca_3N_2$ with (A) no salt added, (B) 2 mol of NH_4Cl added, and (C) 3 mol of NH_4Cl added. The Miller indices for fcc TiN are indicated in A. A, B, and C have calculated particle sizes of >200, 49.1, and 30.8 nm, respectively.

and/or metal impurities. The synthesis of phase-pure TiN proved difficult using either $TiCl_3$ or TiI_4 precursors with Li_3N, as Ti metal impurities were found in the products. To mitigate the insufficient nitridation problem, 1 mol of NaN_3 was used to replace one-third of a mole of Li_3N in the reaction with $TiCl_3$ as given in eq 1. This large excess of nitrogen proved favorable to forming phase-pure cubic titanium nitride.[23]

$$TiCl_3 + {}^2/_3Li_3N + NaN_3 \rightarrow TiN + NaCl + 2LiCl + 2{}^2/_3N_2 \quad (1)$$

However, because of their volatile/explosive nature, azides are not ideal for controlling the temperature of highly exothermic metathesis reactions. Hence, calcium nitride (Ca_3N_2),which has proven successful in the synthesis of other nitrides, was used as an alternative to the Li_3N/NaN_3 nitriding agents. Previous research has demonstrated that when Ca_3N_2 replaces Li_3N, more energetic, higher temperature reactions ensue, enabling phase-pure TiN to be produced (Figure 1a).[21,24] This synthetic reaction is given in eq 2.

$$TiCl_3 + 0.5Ca_3N_2 \rightarrow TiN + 1.5CaCl_2 \quad (2)$$

Least-squares refinement of the X-ray powder diffraction peaks indicates that the lattice parameter of the TiN (4.2473 Å) synthesized from $TiCl_3$ and Ca_3N_2 closely matches the reported literature value (4.2331 Å) (JCPDS 38-1420). Thermogravimetric analysis was carried out by heating in air from room temperature to 1500 °C, to convert the TiN into TiO_2. A typical TGA of the TiN indicates a ratio of Ti:N of 1:0.92. Powder X-ray diffraction indicates that in addition to the expected TiO_2, some TiO is present in the product. Therefore, the nitrogen value should be considered a lower limit to the nitrogen content of the sample. The addition of up to 3 mol of salt as diluents to this reaction still produces phase-pure TiN without the need for azides, as observed by X-ray powder diffraction (Figure 1b, c). Thus, the $TiCl_3/Ca_3N_2$ reactant system is useful for studying the effects of diluents on reaction temperature, crystallite size, and surface area.

Table 1. BET Surface Areas and Calculated Crystallite Sizes for TiN Produced by Metathesis Reactions with and without Salt Additives

reaction	reaction size (g)	crystallite size (nm)	surface area (m^2/g)
$2TiCl_3 + Ca_3N_2$	1.00	>200	16
$2TiCl_3 + Ca_3N_2 + 1NH_4Cl$	1.00	>200	24
$2TiCl_3 + Ca_3N_2$	0.25	>200	53
$2TiCl_3 + Ca_3N_2 + 1NH_4Cl$	0.25	100.9	
$2TiCl_3 + Ca_3N_2 + 2NH_4Cl$	0.25	49.1	60
$2TiCl_3 + Ca_3N_2 + 3NH_4Cl$	0.25	30.8	71

Different salt diluents were tested next in the reaction between $TiCl_3$ and Ca_3N_2 to determine which works best. LiCl, $CaCl_2$, $NaNH_2$, and $LiNH_2$ additives all suffer from either subnitride formation or titanium metal impurities. When powder X-ray diffraction was used as a screening tool, only NH_4Cl was found to maintain phase homogeneity when up to 3 mol was added (Figure 1c).

Changes in average crystallite size can be monitored using powder X-ray diffraction via line broadening. The Scherrer formula ($t = 0.9\lambda/(B \cos \theta_B)$), compares the additional breath, B, of the TiN peak at an angle θ_B to an internal silicon standard. The addition of 1−3 mol of NH_4Cl was found to have a dramatic effect on crystallite size (Table 1). The crystallite size can be reduced from >200 nm in the direct reaction between $TiCl_3$ and Ca_3N_2 (Figure 1a) to 30.8 nm with the addition of 3 mol of ammonium chloride (Figure 1c). Microscopy experiments were preformed on the TiN product to confirm the data found through powder X-ray diffraction. As expected, TiN samples in which no salt diluents were added into the reaction mix produced micrometer-sized particles, as observed by scanning electron microscopy (Figure 2). When 3 mol of NH_4Cl is added to the $TiCl_3/Ca_3N_2$ reaction, 20−30-nm-sized particles are observed by transmission electron microscopy (Figure 3). This is consistent with the crystallite size calculations based on the Scherrer formula.

In situ temperature measurements were carried out to better understand the changes in crystallinity with salt additives (Figure 4). Most of the driving force for metathesis reactions comes from the high lattice energy of the ionic salt byproduct. Assuming complete reaction and adiabatic conditions, the maximum reaction temperature (denoted $T_{max,calc}$) can be calculated for any metathesis reaction. For the neat reaction of $TiCl_3 + 0.5Ca_3N_2$, theory predicts a $T_{max,calc}$ of 1935 °C. This theoretical value can be compared to the measured value of 1710 °C recorded for a 0.25-g reaction between $TiCl_3$ and 0.5 Ca_3N_2 (Figure 4, leftmost curve). Because typical yields for this synthesis are >90%, the lower measured temperature compared to the calculated tem-

---

(23) Gillan, E. G.; Kaner, R. B. *Inorg. Chem.* **1994**, *33*, 5693−5700.
(24) Hector, A. L.; Parkin, I. P. *Chem. Mater.* **1995**, *7*, 1728−1733.

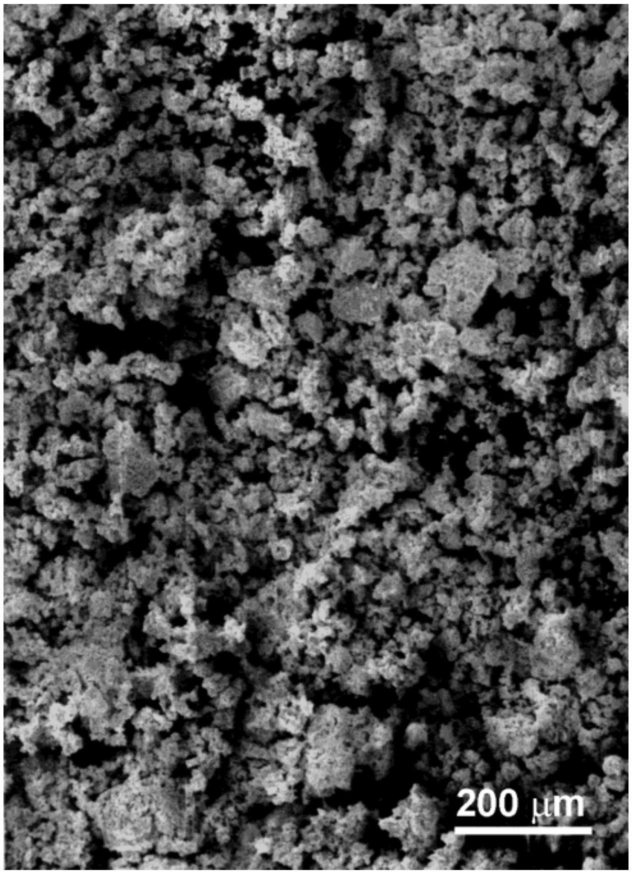

Figure 2. SEM image of the washed TiN micrometer-sized particles produced in a reaction between $TiCl_3$ and Ca_3N_2.

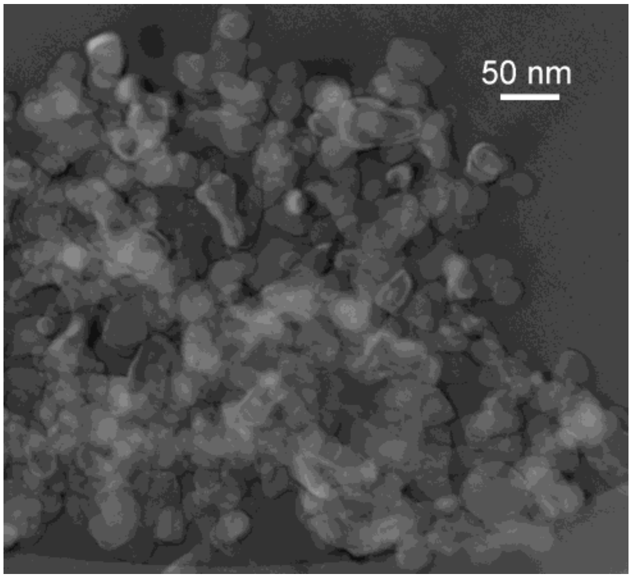

Figure 3. TEM image of the TiN produced from the reaction of $TiCl_3 + Ca_3N_2 + 3NH_4Cl$. The 20−30-nm size range of the particles is consistent with the average crystallite size of 30.8 nm calculated from the X-ray diffraction pattern (Figure 1c).

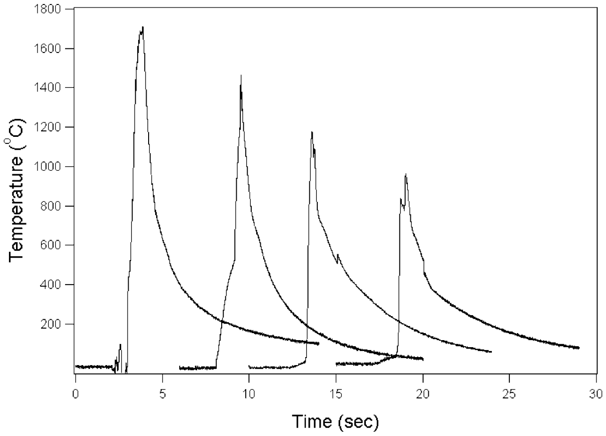

Figure 4. T_{max} measurements of 0.25-g reactions between $TiCl_3 + 0.5Ca_3N_2$ with, from left to right, 0 mol of NH_4Cl added, 1 mol of NH_4Cl added, 2 mol of NH_4Cl added, and 3 mol of NH_4Cl added.

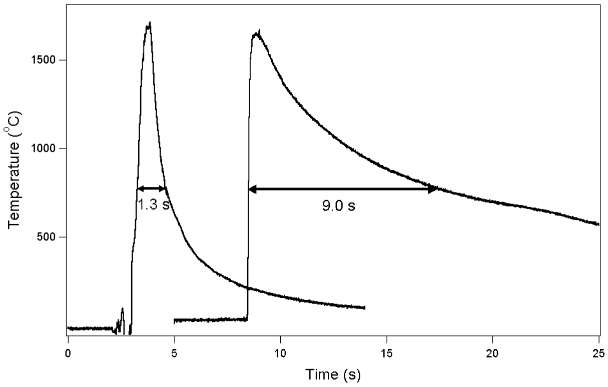

Figure 5. In situ T_{max} measurements of reactions between $TiCl_3$ and $0.5Ca_3N_2$ to produce 0.25-g (left) and 1.0-g (right) yield. The arrows depict the amount of time the reactions stay above the melting point of the byproduct salt $CaCl_2$.

perature can be mainly attributed to nonadiabatic conditions. Previous experiments with other nitrides have found that by using a thermally insulating reactor, measured reaction temperatures significantly increase and can approach theoretical predictions.[21]

When ammonium chloride is added to the $TiCl_3/Ca_3N_2$ reaction mixture, the T_{max} of the reaction is expected to decrease. This can be seen in Figure 4 where the $T_{max,exp}$ values drop from 1710 to 1463, 1178, and 965 °C as 1, 2, and 3 mol of NH_4Cl are added. With the addition of 4 mol of NH_4Cl, the reaction between $TiCl_3$ and $0.5Ca_3N_2$ will no longer propagate. This is consistent with the T_{max} calculation, which indicates that the reaction is no longer exothermic, as more energy is needed to sublime the NH_4Cl than can be supplied from the reaction.

To further corroborate the control over crystallite size of the TiN product, surface area measurements were performed via nitrogen gas absorption (BET). Two methods were found to control surface area, first diluents and second reaction size. Both depend on heat dissipation of the reaction mix. Reactions to produce 1 g of TiN yield a surface area of 16 m^2/g. Keeping the reaction scale at 1 g of TiN while adding 1 mol of ammonium chloride increases the surface area of the product by 50%, to 24 m^2/g. A more dramatic effect occurs when the reaction scale is reduced 4-fold to produce 0.25 g of TiN without diluent. The 0.25-g reaction yields TiN with a surface area of 53 m^2/g, a 350% increase from the 1-g reaction. This effect can be understood by further comparison of the in situ temperature profiles (Figure 5). For every 1 g of TiN produced, 2.7 g of $CaCl_2$ also form, releasing a great deal of heat (−9.5 kJ). For nearly 10 s (Figure 5, right), the reaction mixture remains above the melting point of the $CaCl_2$ byproduct salt (775 °C), enabling crystal growth to proceed via Ostwald ripening.[25] Correspondingly, this lowers the surface area. By simply changing the reaction scale to produce only 0.25 g of TiN, only 0.67 g of $CaCl_2$ form, releasing −2.4 kJ of heat. This in turn reduces the amount of time that the reaction mix spends above the melting point of the byproduct salt to just over 1 s (Figure 5, left). Hence, the surface area increases to 53 m^2/g. With the addition of diluents such as 2 mol of NH_4Cl, the surface area can be further increased to 60 m^2/g. Through the addition of 3 mol of NH_4Cl, the surface area is raised to 72 m^2/g since now the reaction mix remains above 775 °C for only 0.6 s. Further addition of NH_4Cl results in nonpropagating reactions.

Since titanium nitride is expected to possess a relatively high electrical conductivity and be chemically inert, TiN produced by metathesis reactions is a good candidate for testing as supercapacitor electrodes. TiN made from $TiCl_3$ and Ca_3N_2 with a surface area of 24 m^2/g was used as both the cathode and anode in capacitance cells with concentrated potassium hydroxide as the electrolyte. After sealing the electrodes within a silicone gasket, the cells were tested and found to have low equivalent series resistances (ESR) of <100 mΩ and relatively high capacitances of >100 F/g (>500 F/cm^3). RC (resistive-capacitive) time constants from μs to 1 s were observed with energy densities of >10 W·h/kg and Coulombic efficiencies near 100%. The TiN electrodes were found to be very stable in the concentrated potassium hydroxide electrolyte and 10^6 cycles were achieved with minimum passivation of the electrodes. Comparable experiments with commercially available TiN indicate that the TiN synthesized via metathesis reactions is superior in performance when used as capacitor electrodes. Experiments are planned to scale up the syntheses and measure the capacitance of the higher surface area materials.

Conclusions

Reduction of reaction size used in conjunction with the addition of NH_4Cl as a diluent is shown to be a fast, reliable method for controlling particle size and surface area of TiN. These methods reduce the amount of time the product remains in a molten salt melt and therefore arrests the growth of TiN crystallites. Calculations of crystallite size from powder X-ray diffraction are supported by both SEM and TEM data. In addition, BET measurements confirm that as crystallite size decreases, surface area increases. Experiments testing the TiN product as electrodes in supercapacitors find a relatively high capacitance (>100 F/g) and a Coulombic efficiency approaching 100% even after a million charging and discharging cycles. This method of controlling surface area and particle size is thought to be general and should be applicable to other metathesis reactions.

Acknowledgment. The authors would like to thank Madeleine A. Low for her help in running metathesis reactions. This work was supported by the National Science Foundation Grant # 0073581.

CM034629N

---

(25) Baldan, A. *J. Mater. Sci.* **2002**, *37*, 2171−2202.