Electrochemical Synthesis of Ceramic Materials. 5. An Electrochemical Method Suitable for the Preparation of Nine Metal Nitrides

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We discuss an electrochemical approach suitable for preparing nine metal nitride precursors and the corresponding metal nitrides. The method involves anodic dissolution of a metal electrode in a single-compartment electrochemical cell containing an electrolyte solution consisting of liquid NH_3 and NH_4X (X = Br or Cl). Following evaporation of the solvent and calcination of the resulting powder at temperatures between 375 and 1100 °C, we obtain the metal nitride corresponding to the anode material. Using this approach metal nitride ceramic powders corresponding to Al, Ga, Mo, Nb, Ni, Ti, V, W, and Zr have been prepared. We also describe a simple modification to the metal nitride synthesis that is suitable for the preparation of composite metal nitride powders. The ceramic materials were characterized primarily by powder X-ray diffraction. The calcination conditions determine the resulting phase, composition, and morphology of the product. For example, when Ar is used to calcine the Mo nitride precursor Mo_2N obtains, but when NH_3 is the calcination gas we obtain MoN. Calcination of the precursors at different temperatures results in ceramic powders having different phases.

Introduction

Because of their commercial and technological importance, there is interest in developing new synthetic approaches for preparing metal nitrides and improving on those presently in use. The two most common routes to transition-metal nitrides are carbothermal reduction of the metal oxide and direct nitridation of the metal in NH_3 or N_2.[1−6] However, these approaches generally require very high reaction temperatures, and the reactions are often incomplete, which can result in O and C contamination. Such contaminants tend to degrade the electronic, thermal, and mechanical properties of the materials. Some other approaches to metal nitride powder synthesis are transferred-arc plasma synthesis,[7] aerosol reactor synthesis,[8] direct reaction of the metal halide with liquid NH_3,[9] and anodic dissolution of the metal in an organic amine solution.[10−17] The latter two techniques are closely related to the strategy we describe here.

In this article we demonstrate that the anodic dissolution of each of nine metals in a liquid NH_3 electrolyte solution results in formation of inorganic precursors that can be calcined to yield the corresponding metal nitrides. This electrochemical synthetic method is a simple approach to preparing Al, Ga, Mo, Nb, Ni, Ti, V, W, and Zr metal nitrides. We also describe a simple modification to this approach that is suitable for the preparation of composite metal nitride powders. Our approach is both environmentally friendly, in that the only significant byproduct that cannot be recycled into the process is H_2, and it is inherently free of O and C, which are common impurities in metal nitrides. The goal of the present work is to qualitatively demonstrate the feasibility and generality of this electrosynthetic approach; little emphasis is placed on optimization or a detailed analysis of the resulting ceramic powders.

Although our electrosynthetic approach for preparing each of the nine metal nitride powders is similar, the materials themselves are quite different. Al and Ga are not transition metals, and their nitrides are covalent compounds. Ni is a late transition metal.[5] The remaining materials are early transition-metal interstitial alloys.[5,18] The electrochemically prepared precursors are also quite distinct from one another even though

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the experimental approach used to prepare them is nearly identical.

Experimental Section

Precursor Synthesis. As described previously, the electrochemical reactions were conducted in an 80 mL single-compartment, two-electrode glass cell configured for vacuum line operation.[19−22] The cell contained two 0.025 or 0.050 cm thick metal-foil electrodes (Johnson-Mathey: Ga, 99.998%; Fe, 99.9+%; Mo, 99.95%; Ni, 99.7%; Ti, 99.5%; V, 99.8%; W, 99.8%; and Zr, 99.8%). The electrodes were either configured as concentric cylinders, with the anode on the outside (Fe, Mo, Ni, and W), or as parallel sheets (Ga, Ti, V, and Zr). The Ga electrodes were formed by melting the Ga metal into a Plexiglas mold and then freezing the metal with liquid N_2. The anode and cathode areas are 42.5 and 25.0 cm^2/side, respectively, for the concentric arrangement, and 12.5 cm^2/side in the parallel configuration. Current densities reported in the text take into account only one side of the anode. The electrode separation in both the parallel-plate and concentric-circle configurations was typically about 0.5 cm. Before each electrolysis, the electrodes were washed with soap and water and then rinsed with deionized water and ethanol.

NH_4Br (Merck) was used as the electrolyte for all electrochemical experiments, except NH_4Cl (Merck) was used for the Ni electrolysis since it sublimes at a lower temperature than NH_4Br, which enhances recovery of the Ni_3N product. Prior to each experiment the electrolytes were dried for 1 h in a vacuum oven at 80 °C and then added to the cell. The cell was attached to a glass, diffusion-pumped, vacuum line and evacuated to a pressure of $(1-5) \times 10^{-4}$ mmHg. Finally an appropriate volume of Na-purified anhydrous-grade NH_3 (Matheson) was condensed into the electrochemical cell.[19−23]

The electrolyses were performed for 0.5−6 h using a Lambda Model LLS-9000 constant-current power supply or a Sorensen Model DCR 150-3B constant-current source (Raytheon Co.). The cell was immersed in a dry ice/2-propanol bath at −78 °C during the electrolyses. However, the electrolyte solution was not stirred nor was its temperature directly measured. Since the current is high in these experiments, we anticipate some resistive heating of the electrolyte solution. The voltage was measured between electrodes using a Keithley Model 197A autoranging microvolt digital multimeter and recorded as a function of time on a Kipp and Zonen Model BD-90 $X-Y$ recorder.

Following each electrolysis, the liquid NH_3 was allowed to evaporate through a Hg bubbler and then physisorbed NH_3 was removed by evacuating the cell overnight at 25 °C. Before removal of the precursor powder, the contents of the cell were isolated from the laboratory air, disconnected from the vacuum line, and placed in a N_2-containing drybox to prevent oxygen contamination. The precursor powder, which consists of the ceramic precursor, unreacted electrolyte, and other electrolysis products, was collected from the cell by scraping the walls with a stainless-steel spatula. It was then transferred to a quartz boat for subsequent calcination.

Calcination. Quartz boats containing the precursor powder were placed in gastight quartz calcination tubes and removed from the drybox. The tube was then placed in a calibrated Lindberg Model 55035 tube furnace, and the precursor powder was exposed to flowing, high-purity Ar or NH_3 gas (600 mL/min), which was further purified by passing over finely dispersed Na metal.[23] The furnace temperature was ramped to the maximum calcination temperature at 5 °C/min, held for 2 h, and cooled to 25 °C at 20 °C/min. After calcination, the tube was transferred back to the drybox and the metal nitride product removed for analysis. All yields are given in terms of the molar percentage of the metal or metal ions converted to the corresponding nitride unless otherwise stated.

Characterization. The calcined metal nitride ceramics were characterized by X-ray powder diffraction using a Scintag PAD V diffraction system (Cu $K\alpha_1$ line, Ni filter, Be window, with stepped scan (0.025°/step, 3 s/step)).

Results and Discussion

Single-Component, Metal Nitride Syntheses. We have already discussed the electrochemical synthesis of AlN and NbN precursors in detail.[19−22] The pathways that lead to these two materials are quite different even though the experimental methods are the same. The AlN precursor requires generation of NH_2^- at the cathode and Al^{3+} at the anode. We have speculated that these two components combine to eventually yield an inorganic polymer containing only Al, N, and H.[21] The NbN precursor also requires anodic dissolution of the metal anode, but in this case Nb^{5+} reacts directly with liquid NH_3 by ammonolysis to form the ceramic precursor.[22]

Ga. GaN has a hexagonal structure and is isomorphic with AlN.[24] GaN shows promise as a material for blue-light-emitting diodes, photodetectors, and ultraviolet lasers, and methods for preparing ultrapure materials are currently the object of intense research.[25]

Unlike the Nb halides, Ga halides do not undergo ammonolysis in liquid NH_3.[26] This suggests that the electrochemically synthesized GaN precursor forms by a pathway similar to that of AlN.[21] The voltage vs time curve for constant-current electrolysis of Ga in liquid NH_3/NH_4Br rises continuously until it reaches 100 V (Figure 1a). Even at this high value, the current drops to near zero by the end of the electrolysis, which indicates electrode passivation or a very large increase in solution resistance. The higher-than-theoretical yield for the anode loss per charge consumed (Table 1, column 7) indicates that reactions other than simple metal oxidation occur at the anode. The XRD spectrum of the GaN precursor calcined at 950 °C in NH_3 is consistent with the JCPDS card file for this material, which indicates that the only crystalline material present is GaN (Figure 2).[24]

Mo. MoN and Mo_2N are interstitial alloys.[5] MoN is generally prepared by direct nitridation of the metal in N_2 or NH_3 gas or by reduction of the oxide in NH_3 gas at elevated temperatures.[3,5] Mo_2N results when N diffuses out of the MoN lattice during high-temperature calcination. MoN has a hexagonal crystal structure, and Mo_2N has a cubic crystal structure. Mo_2N is used as a

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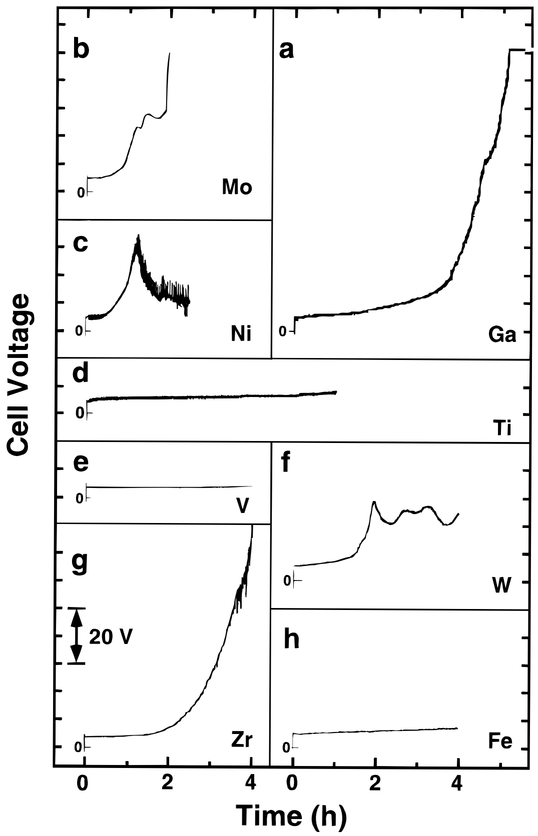

Figure 1. Voltage vs time curves for anodization of (a) Ga, (b) Mo, (c) Ni, (d) Ti, (e) V, (f) W, (g) Zr, and (h) Fe. The current densities are listed in Table 1.

catalyst in, among others, Fischer–Tropsch, and NH_3 syntheses.[3]

The electrolysis of Mo in liquid NH_3 produces a pink solution that grows darker as the experiment proceeds. The coloring of the solution could be due to $MoBr_2$, which is a yellow-red compound, or $MoBr_3$, which forms a deep red solution in liquid NH_3.[27,28] Gas evolution occurs at the cathode during electrolysis, but it decreases with time due to loss of the electrolyte.[21] After electrolysis, a brown powder remains; calcination of this powder yields a black product.

The voltage vs time curve for the Mo electrolysis begins at 5 V and after 2 h exceeds 50 V (Figure 1b). Two maxima, which appear at about 1.0 and 1.5 h, may result from an unstable passivating film or a change in the anode reaction. The dramatic increase in voltage at the end of the electrolysis probably indicates electrode passivation, but it could also be associated with a rapid increase in solution resistance arising from electrolysis of the electrolyte.

The calculated yield of MoN based on anode weight loss (Table 1, column 12) is 130%. This indicates that the product is not pure nitride, and since the XRD spectrum of the MoN does not indicate another crystalline phase, the impurity must be amorphous. Since elemental analysis was not performed on the Mo product, we can only speculate that the contaminant contains Br as a principal component in analogy to the

Table 1. Electrolysis Data

1 anode	2 anode mass loss (g)	3 anode area (cm^2)/current density[a] (A/m^2)	4 electrolysis time (h)	5 anode loss (equiv) [oxidation state][b]	6 charge consumed by cell (equiv)	7 anode loss/charge consumed (equiv/equiv)	8 precursor mass (g)	9 precursor mass before Calcination (g) [ambient/temp (°C)]	10 product mass after calcination (g)	11 yield of product from precursor (%)	12 yield based on anode mass loss[c] (%)
Ga	1.9963	12.5/130	6.0	0.086 [3]	0.070	1.23[d]	4.1403	4.1403 [NH_3/700]	1.2673	31	53
Mo	0.4668	42.5/180	2.0	0.015 [3]	0.057	0.26	2.0525	0.9764 [Ar/800]	0.3398	33	130[e]
Ni[f]	0.8827	42.5/150	2.7	0.030 [2]	0.064	0.47	2.7742	0.3150 [NH_3/375]	0.0980	31	91
Ti	0.4941	12.5/280	6.0	0.031 [3]	0.077	0.40	1.3613	1.3613 [NH_3/1100]	0.5028	37	79
V	0.0488	12.5/150	4.0	0.003 [3]	0.028	0.10	3.2476[g]	3.2476[h] [NH_3/600]	0.2181[h]	6.7	86
W	0.6612	42.5/180	4.0	0.022 [6]	0.113	0.19	2.1482	0.8081 [NH_3/600]	0.2430	30	91
Zr	0.7640	12.5/150	4.0	0.025 [3]	0.028	0.89	2.4681	2.3503 [NH_3/1100]	0.6916	29	88
Fe	0.5139	42.5/150	4.0	0.028 [3]	0.096	0.29	1.7130	1.7130 [Ar/600]	1.0291	60	*h*

[a] Based on one side of the anode. [b] Oxidation state assumed (see ref 39) for anode loss calculation. [c] These values are based on conversion of all of the anode weight loss into the corresponding metal nitride. [d] The Ga anode spontaneously dissolved in the electrolyte solution, and since it was not convenient to separate this mass loss from that due to anodic dissolution this value represents the total loss from both channels. [e] Excess mass may be caused by Br contamination. [f] NH_4Cl electrolyte. [g] Sum of two electrolyses. [h] Product not determined.

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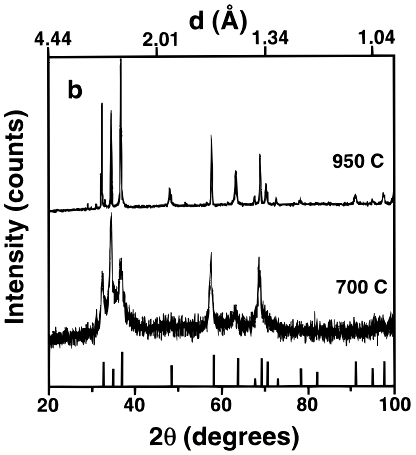

Figure 2. XRD spectra for the electrochemically synthesized GaN precursor calcined at two temperatures in flowing NH_3. The JCPDS file-card pattern is shown at the bottom of the figure.[24]

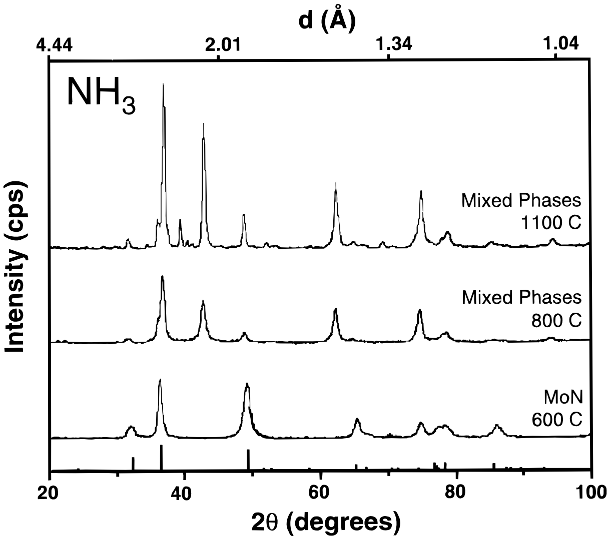

Figure 3. XRD spectra of the Mo nitride precursor calcined at different temperatures in flowing NH_3. The JCPDS file card pattern for MoN is shown at the bottom of the figure.[24]

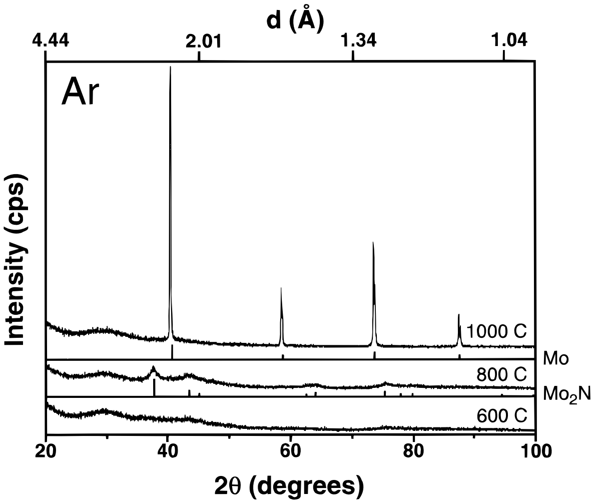

Figure 4. XRD spectra of the Mo nitride precursor calcined at different temperatures in flowing Ar. The JCPDS file card pattern for Mo_2N (800 °C) and Mo (1000 °C) are shown below each spectrum.[24]

elemental composition of electrochemically prepared NbN.[22]

Calcination conditions often determine the chemical and physical properties of metal nitrides. For example, the calcination gas and temperature determine the purity and morphology of AlN[21] and the phase of NbN.[22] Figures 3 and 4 illustrate this same behavior for the product of the MoN precursor calcination. When the precursor is calcined in NH_3 at 600 °C, MoN results, but heating to higher temperatures yields mixed phases we could not identify (Figure 3).[24] XRD spectra of the Mo nitride precursor calcined in Ar at 600, 800, and 1000 °C are shown in Figure 4. The spectrum of the product calcined at 600 °C indicates no diffraction maxima suggesting that it is an amorphous material. The diffraction pattern at 800 °C has small, broad diffraction maxima arising from Mo_2N, and the pattern obtained by calcining at 1000 °C corresponds to Mo metal.[24] The barely detectable peak splitting at high 2θ for the precursor calcined at 1000 C in Ar is due to $K\alpha_2$ X-rays from the Cu X-ray source. The phase changes of the powders at different temperatures indicate diffusion of N from the powders to the flowing gas ambient, and the differences in the products that result from calcining in Ar and NH_3 ambients underscore the nitriding ability of NH_3 at high temperatures.[29]

Ni. Ni_3N is a late transition metal, but it is also an interstitial alloy with N occupying interstices in the Ni lattice.[18] Ni_3N can be prepared by the reaction of KNH_2 and Ni salts in liquid NH_3 followed by heating the resulting $Ni(NH_2)_2 \cdot 2NH_3$ in vacuum to 362 °C, by heating Ni metal in N_2 gas at 585 °C, or by passing a rapidly flowing stream of NH_3 over Ni powder.[18] Although technological applications of Ni_3N are limited, Fe–Ni nitride alloys have better magnetic properties and corrosion resistance than pure Fe.[30]

The voltage vs time curve for the Ni electrolysis (Figure 1c) is similar to that found for Al.[21] However, after the maximum in cell voltage obtains, the voltage becomes so erratic that the electrolysis was discontinued. Gas evolution was apparent as soon as current was applied to the cell, but after ~30 min the solution turned pink and gas evolution nearly ceased. Toward the end of the electrolysis a light-pink material coated the anode and a black compound adhered to the cathode. A light purple powder remained after evaporation of the solvent. The pink color probably corresponds to $[Ni(NH_3)_6]Br_2$, which is violet.[28] The black deposits on the cathode are probably electrodeposited Ni.[31,32]

Calcination of the NiN precursor powder at 600 °C in flowing Ar results in a tan powder, but XRD analysis indicates that it is amorphous. It is likely that calcination of the Ni precursor results in decomposition of the nitride. For example, when $Ni(NH_2)_2$ is heated briefly to 120 °C in vacuum it yields Ni_3N_2, but it decomposes after prolonged heating at 120 °C.[27,33]

Electrolysis of Ni in a NH_4Cl-containing electrolyte solution (Figure 5a) results in a different voltage vs time curve than we observed for the NH_4Br electrolyte

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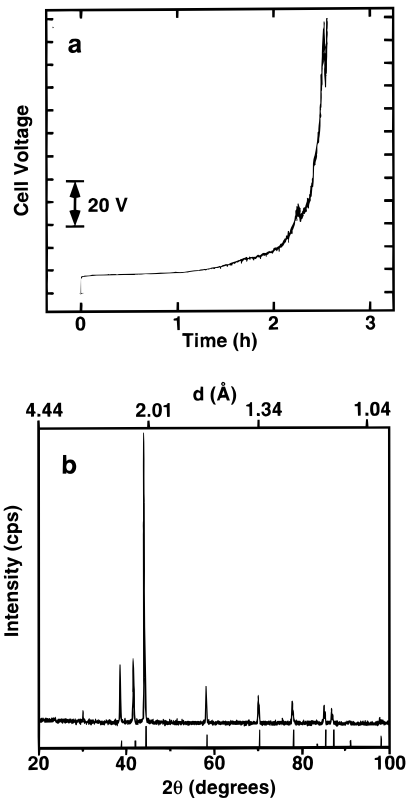

Figure 5. (a) Voltage vs time curve for the Ni electrolysis performed in an NH_4Cl-containing electrolyte. (b) Powder XRD spectrum of the Ni precursor after calcination in flowing NH_3 at 375 °C. The JCPDS file card pattern for Ni_3N is shown below the XRD spectrum.[24]

solution (Figure 1c). The higher final voltage observed in the Cl$^-$-containing electrolyte solution, compared with the Br$^-$ electrolyte solution, might be indicative of electrode passivation since both the anode and cathode were covered with purple and black deposits, respectively, at the end of electrolysis in the Cl$^-$-containing electrolyte.

Calcination of these deposits at 375 °C, along with the purple and black precipitate remaining in the bottom of the cell after NH_3 evaporation, results in the formation of Ni_3N (Figure 5b).[24] Apparently the lower sublimation temperature of NH_4Cl (340 °C compared to 452 °C for NH_4Br) allows recovery of the ceramic product prior to decomposition.

Ti. TiN is another interstitial alloy.[5] TiN can be prepared by direct nitridation of the metal in N_2 or nitridation of $TiCl_4$ at elevated temperatures.[5] Preparation of TiN coatings using CVD methods are also well established.[34] TiN is a metallic ceramic with a golden luster, and it has a cubic crystal structure. It is used for wear resistance coatings and as an inexpensive stand-in for Au in the jewelry industry.[34]

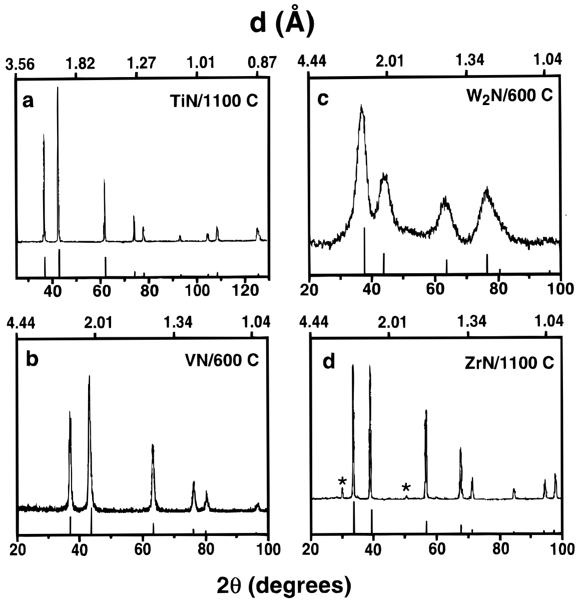

Figure 6. XRD spectra of the metal nitride ceramic powders obtained from electrochemically synthesized precursors: (a) TiN, (b) VN, (c) W_2N, and (d) ZrN. The asterisks indicate unidentified phases. The JCPDS file card pattern for each compound is shown below the appropriate spectrum.[24]

The voltage vs time curve for a constant-current electrolysis of Ti in liquid a NH_3/NH_4Br electrolyte solution showed little change during the 6 h experiment (Figure 1d). This indicates little change in the solution conductivity and little or no passivation of the electrodes. At the beginning of the Ti electrolysis the solution turns yellow but then becomes green, possibly due to the presence of a blue $e^-_{NH_3}$ solution mixing with the otherwise yellow solution.[21] In a study by Gill et al., anodic dissolution of Ti in a liquid NH_3/NH_4BF_4 electrolyte solution produced a pale yellow compound, but they did not report the structure of this material.[32] Like Nb,[22] Ti salts undergo spontaneous ammonolysis in liquid NH_3 and the TiN precursor likely forms by a route similar to the NbN precursor.[26] An XRD spectrum of the precursor powder calcined in NH_3 at 1100 °C indicates that the only crystalline material present is TiN (Figure 6a)[24] and elemental analysis of the powder reveals it to be nearly stoichiometric TiN (Ti/N = 0.95).[20]

V. VN is another interstitial alloy.[5] VN powders can be prepared by nitridation of the metal, or a metal salt, with N_2 or NH_3 at elevated temperatures. Coatings can be prepared by chemical vapor deposition (CVD).[5,34] VN has a cubic crystal structure[5] and is used as a catalyst for the synthesis of NH_3 and as a wear-resistant coating.[4]

The electrolysis of V electrodes results in almost no time-dependent change in cell voltage (Figure 1e). At the beginning of the electrolysis the solution turns brown, and then it becomes progressively darker. In another study, it was found that electrolysis of V in a NH_4BF_4/liquid NH_3 solution produced brown deposits on the anode, but they were not characterized.[32] Little of the anode is oxidized and the anode loss per charge consumed (Table 1, column 7) is very low. However, the yield based on anode weight loss is high (Table 1, column 12). V is another transition metal whose soluble halide salts undergo spontaneous ammonolysis in liquid NH_3, and therefore precursor formation probably does not rely upon cathodic generation of NH_2^-.[26] XRD indicates that the sole crystalline calcination product of the precursor is VN (Figure 6b).[24]

W. Like the other early transition-metal nitrides, W_2N is an interstitial alloy, and like many of these compounds it has a cubic crystal structure.[5] W_2N powders can be prepared by nitridation of the metal or a metal salt with N_2 or NH_3 at elevated temperatures,

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and coatings can be prepared by CVD.[5,34] W_2N is a catalyst for the synthesis of NH_3.[35]

As for the Mo electrolysis, the W electrolysis in liquid NH_3 reveals multiple maxima in the voltage vs time curve (Figure 1f); however, the maximum voltage attained is much smaller than for the Mo experiment. Application of current to the cell causes the solution to turn yellow, but it is red by the end of the experiment. In the study by Gill et al., anodic dissolution of W in NH_4BF_4/liquid NH_3 electrolyte resulted in an orange precipitate at the anode; however, they did not characterize this material.[32] Soluble halides of W, such as WCl_6, undergo ammonolysis in liquid NH_3, so we expect that the reaction pathway that leads to the precursor is similar to that of Nb or V.[26] The XRD spectrum of the calcination product shows diffraction maxima corresponding to W_2N, and the broad peaks indicate that the average crystallite size is in the nanometer range (Figure 6c).[24,36]

Zr. ZrN is yet another interstitial alloy with a cubic crystal structure.[5] ZrN powders can be prepared by nitridation of the metal or a metal salt with N_2 or NH_3 at elevated temperatures, and coatings can be prepared by CVD.[5,34] ZrN is used commercially for wear-resistance coatings.[34,35]

The voltage vs time curve for the Zr electrolysis increases very slowly for the first 2 h, but it rapidly increases to >80 V during the final 2 h (Figure 1g). At the start of the electrolysis the solution turns pink, and there is significant gas evolution, but the solution eventually turns purple and gas evolution slows. We recovered a gray powder after electrolysis and then calcined it at 1100 °C in NH_3. Like, Nb, Zr halides can undergo ammonolysis in liquid NH_3, so the yield of ZrN calculated from the anode loss is high (Table 1, column 12). The XRD pattern of the powder calcined at 1100 °C in NH_3 corresponds to ZrN (Figure 6d).[24]

Fe. Like Ni, Fe is a late transition metal and N is less soluble in the Fe metal lattice than in the early transition metals. Fe has a number of nitride phases.[18] Fe nitrides can be prepared by flowing NH_3 over Fe powder at 450 °C or by treatment of $FeBr_2$ with K in liquid NH_3 at -33.5 °C.[18] Fe nitride compounds are hard magnetic materials.[37]

Like the Ti and V electrolyses, the voltage vs time curve for the Fe electrolysis indicates little change during the experiment (Figure 1h). There is gas evolution at the electrodes, especially around the cathode, and then the solution turns progressively more brown. By the end of the electrolysis, gas evolution slows considerably. Anodic dissolution of Fe in NH_4BF_4/liquid NH_3 electrolyte yielded a brown cathode deposit that was referred to as an amido complex in a study similar to that discussed here.[32] In this previous work, the amount of metal oxidized per charge consumed was reported as being low due to N_2 evolution at the anode.[32]

A black and white powder remains after evaporation of NH_3. Calcination of this material at 600 °C in Ar results in a brown powder. The XRD pattern of this material indicates diffraction maxima only for $FeBr_2$ and $FeBr_3$. Therefore, we believe the relatively unstable Fe nitride decomposes during calcination.[5] Salts of Fe react directly with KNH_2 in liquid NH_3 to form FeN without heating.[38] This suggests that in our experiment FeN forms in the bulk electrolyte solution rather than being tied to electrode processes other than anodic dissolution of the Fe anode.

Table 2. Compositional Data for Al/Ti Composite Nitrides

Al/Ti anode time	1/1	2/5	5/2
Al mass loss (g)	0.2461	0.1645	0.4138
Ti mass loss (g)	0.1689	0.2866	0.1674
Al lost (mmol)	9.1	6.1	1.5
Ti lost (mmol)	3.5	6.0	3.5
Al/Ti (moles lost/moles lost)	2.6	1	4.3
Al in product (%)	37.0	34.2	38.2
Ti in product (%)	32.3	38.4	22.8
N in product (%)	28.1	27.0	26.5
total (%)	97.4	99.6	98.5
Al/Ti mole ratio in product	2.1	1.6	3.1

Composite Nitride Syntheses. Composites of AlN and TiN can be prepared by repeatedly switching the polarity of the electrodes in a cell containing an Al electrode and a Ti electrode, each with equal areas (12.5 cm^2/side). We varied the amount of time that the Al electrode was the anode to determine the effect on product composition. First, the Al electrode was the anode for 1 min periods and the Ti electrode was the anode for 1 min periods (Table 2, column 2). Next the Al electrode was the anode for 2 min intervals and the Ti electrode was the anode for 5 min (Table 2, column 3). Finally the Al electrode was the anode for 5 min and the Ti electrode was the anode for 2 min intervals (Table 2, column 4). The objective of these experiments was to determine if the Al/Ti ratio in the resulting precursors and powder tracked the amount of time each metal was the anode. Synthesis of discreet compounds, such as Ti_3AlN, might be possible by choosing the correct cell geometry and stoichiometry of the Al/Ti ratio in the powder, and then calcining at the appropriate temperature for the desired product phase.[39] There is interest in Ti_3AlN because it is very hard and highly abrasive. Discovering new methods for preparing other mixed-metal nitrides is also desirable.

The results of these experiments are shown in Table 2. Although the Al/Ti anode time does not directly reflect the Al/Ti mole ratio in the product, there is a general trend that indicates that the longer a particular metal is the anode, the more of its nitride that remains after calcination. The absence of a direct correlation is not surprising since the anode loss per charge consumed for the Al electrolysis (0.64)[21] is higher than for the Ti electrolysis (0.40) (Table 1, column 7). The mixed-metal precursors were calcined at 1100 °C in flowing NH_3 and analyzed by XRD (Figure 7). The XRD spectrum for this particular experiment clearly shows that the crystalline product is a composite of AlN and TiN rather than a discreet compound or solid solution.

Summary and Conclusion

The electrochemical route to metal nitride materials is quite general, and we have been able to use this approach to synthesize nine different metal nitrides as

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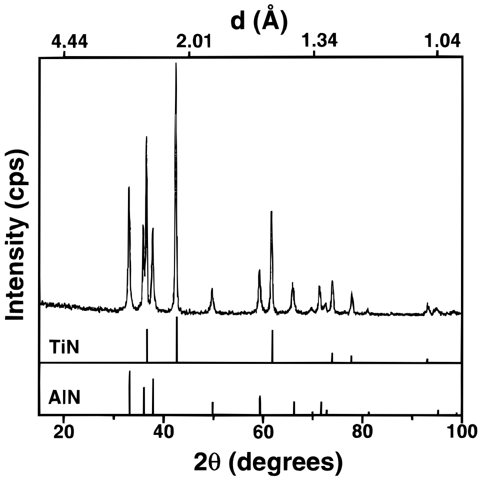

Figure 7. XRD spectra of a mixture of AlN and TiN prepared by calcining a mixed precursor at 1100 °C in flow NH_3. The precursor resulted from continuous reversal of electrode polarity in a cell containing both an Al and a Ti electrode. The Al/Ti anode time ratio for this experiment was 1/1 (see Table 2). The JCPDS file cards for AlN and TiN are shown below the XRD spectrum.[24]

well as a composite Al/Ti nitride material. The nitride of Fe, however, remains elusive. Importantly, we have made little effort to optimize either the electrolysis or calcination steps for any of these materials. Rather, our goal has been to provide a qualitative proof-of-concept study that confirms the generality of this simple synthetic route. In all cases, except Fe, a single set of simple experimental conditions yields the corresponding metal nitride as verified by XRD. In previous, more-detailed studies extensive morphological and elemental analyses were performed.[21,22] These studies showed that varying the calcination temperature affects the surface area and other morphological characteristics of the powders. The experiments discussed here indicate that the calcination temperature and ambient affect the phase of the product.

The greater-than-theoretical yield for the Mo electrolysis suggests Br^- contamination of the calcination product. This problem was also encountered with the Nb electrolysis. When NH_3 is used as the calcination ambient, it reduces electrolyte contamination of the nitride, but this can also change the phase of the product.

Using cathodes that catalyze the cross-reaction between $e^-_{NH_3}$ and NH_3 to form NH_2^- or that have a lower overpotential for NH_3 reduction than $e^-_{NH_3}$ formation could improve the current efficiencies and produce higher yields for the metal nitrides. Materials such as Pt black and Cu have these properties.[40]

The electrolyte used in the electrolysis, as demonstrated by the voltage vs time curves for Ni electrolysis in NH_4Br and NH_4Cl electrolytes, affects the cell reaction and precursor. The use of NH_4Cl, which has a lower sublimination temperature than NH_4Br, enables us to prepare Ni_3N at a significantly lower temperature than the other nitrides. However, this advantage might not be realized in all of these syntheses, since Cl^- salts are less soluble in liquid NH_3 than the corresponding Br^- salts.

The low current efficiencies for oxidation of some of the metals must indicate varying degrees of $e^-_{NH_3}$ formation, which reduces the efficiency of metal dissolution. Yields could be increased by operating the electrolyses at somewhat higher temperatures, since they favor the bulk-phase cross reaction between $e^-_{NH_3}$ and NH_3. Other reactions, such as NH_3 oxidation or metal reduction, could also compete with metal dissolution and reduce current efficiency.

In the synthesis of the Al/Ti composite nitrides, the ratio of Al/Ti is controlled by the ratio of the time each metal is used as the anode in the electrolysis cell. This was a preliminary experiment, and other variables, such as the effect of current density, were not explored. The important points are that it is possible to prepare composites nitrides, and it might eventually be possible to synthesize solid solutions and discreet mixed-metal nitride compounds using this electrochemical approach.

The most important finding to emerge from this study is that a single experimental method yields a broad range of metal nitride materials, even though the reaction pathway differs from metal to metal. It is also significant that product yields are generally high and calcination temperatures relatively low. Additionally, there are no toxic or unrecoverable by-products formed and that the process is inherently O- and C-free. We believe that optimization of this general approach could result in a viable commercial means for preparation of metal nitride powders.

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