

Synthesis of nanoscale particles of Ta and Nb₃Al by homogeneous reduction in liquid ammonia

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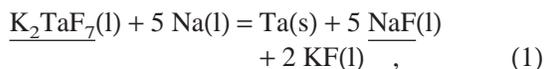
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The analysis of metallothermic reduction as an electronically mediated reaction predicted that the particle size of solid product could be reduced if the reaction were conducted in a medium that is a mixed conductor (ionic and electronic). This prediction was confirmed by reacting TaCl₅ with sodium, each dissolved in liquid ammonia, to produce tantalum powder having an average particle size over an order of magnitude finer than the micron-sized powders produced commercially today. Metallothermic reduction in a mixed conducting medium has been extended to a multicomponent system in order to synthesize nanosized powder of Nb₃Al by co-reduction of NbCl₅ and AlCl₃ both dissolved in liquid ammonia.

I. INTRODUCTION

Reduction in particle size from the current value of around 0.5 μm to something nearer 10 nm would significantly improve the performance of tantalum capacitors. Producing nanoparticles is beyond the capabilities of the current technology that produces tantalum powder by metallothermic reduction in a molten salt medium. At approximately 800 °C, potassium heptafluorotantalate (K₂TaF₇) and sodium are both added to a halide melt (known as a “diluent”) where they react to produce solid tantalum in the form of powder according to



where the underline denotes that the species is dissolved in the diluent. Such a process does not present the conditions necessary to sustain the production of unagglomerated, nanoscale powder. Processing at such a high temperature results in an undesirably high rate of particle growth. The fact that sodium is immiscible in the molten salt diluent promotes heterogeneous nucleation of tantalum on metallic reactor components (wall, stirrer) with attendant agglomeration.

In contrast to the commonly held view that metallothermic reduction is strictly a chemical reaction and that the process is rate limited by mass transfer, previous work in this laboratory had shown that metallothermic reduction is an electronically mediated reaction, i.e., the kinetic pathway necessarily includes an electron transfer step that under certain circumstances is rate limiting.¹

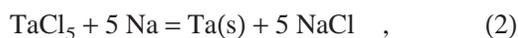
The 2 × 2 matrix in Table I presents a taxonomy of chemical reactions involving precipitation. At first glance all the examples might appear to be simple metatheses or exchange reactions. There are important differences, however.

The rows of Table I sort reactions by whether or not they involve electron transfer: Reactions in the first row do, while those in the second row do not. Hence, first-row reactions proceed necessarily by the transport of both ions and electrons. In some cases, electron transport is fast and the overall rate of reaction is controlled by ion transport. Under these circumstances the reaction kinetics are indistinguishable from those of the conjugate second-row reaction. In other cases involving electron transfer, ion transport is fast, and electron transport is the slow step. These are precisely the conditions that warrant use of the term “electronically mediated.” In the present investigation we show how the control of the electrical properties of the reaction medium can have a dramatic effect on the kinetics which, in turn, affect the nature of the reaction product, e.g., particle size.

The columns of Table I sort reactions according to whether the reactants are present in a single phase or not. In first-column reactions all reactants are present in a single phase. The solid products of such reactions form by homogeneous nucleation. In second-column reactions the reactants are present in a plurality of phases. The solid products of such reactions form by heterogeneous nucleation. Recognition of the differences between the four types of reactions in Table I grants insights into the nucleation and growth kinetics of the formation of the solid precipitate. This, in turn, enables control of particle size.

The production of tantalum powder is a case in point and the focus of the present investigation. Current technology is based upon Reaction (1), which is a heterogeneous reaction involving electron transfer. Because liquid sodium is not soluble in the diluent, the reaction is throttled by the transport of electrons from the sodium to the solvated TaF₇²⁻ anion and is, thus, electronically mediated. This discourages nucleation of small tantalum particles while at the same time favoring particle growth and agglomeration. In parallel, any metal components of the reactor in contact with the reaction medium can serve as nucleation sites for the undesirable deposition of tantalum. The hypothesis of the present investigation was that ultrafine tantalum powder would be produced in a medium in which all reactants are soluble and electron transport is facile. Such a medium would necessarily be a mixed conductor (ionic and electronic). To assess the accuracy of this prediction, the present investigation focused on metallothermic reduction of TaCl₅ in liquid ammonia, a nonaqueous solvent well known for its ability to dissolve alkali metals giving cations and solvated electrons.^{2,3} From the perspective of establishing favorable conditions for making ultrafine powder, metal–ammonia solutions possess ideal electrical properties and are stable at subambient temperatures (low temperatures enhance nucleation and restrain growth). While studies of metallothermic reduction reactions in liquid ammonia have a long history (as far back as 1930 Zintl, Goubeau, and Dullenkopf⁴ reacted lead iodide with sodium dissolved in anhydrous liquid ammonia), there has been no report of conducting reactions in this solvent in order to control the particle size of the product precipitate.

The reaction chosen in the present study for the production of tantalum powder is



where the underline denotes dissolution in liquid ammonia. This reaction is attractive because apart from metallic tantalum all reactants and products are soluble in liquid ammonia. This facilitates separation of the powder product by filtration. In validation of our hypothesis, we show that this reaction produces elemental tantalum with an average particle size over an order of magnitude finer than the micron-sized powders produced

commercially today. We further extended the work to include the simultaneous reduction of multiple salts in order to synthesize powders of intermetallic compounds. To test the extension of Reaction (2) to multicomponent systems, NbCl₅ and AlCl₃ together were reacted with sodium to produce the intermetallic compound Nb₃Al. Last, to show that the finer particle size is not simply due to the temperature effect, we compare the production of copper powder by electronically mediated reactions in two media, one a mixed conductor, the other an ionic conductor.

II. EXPERIMENTAL

A. Chemicals

The chemicals used were sodium metal (Aldrich, 99.9%), TaCl₅ (Alfa Aesar, 99.995%), TaBr₅ (Alfa Aesar, 99.995%), NbCl₅ (Alfa Aesar, 99.995%), AlCl₃ (Alfa Aesar, 99.9995%), CuBr (Alfa Aesar, 99.998%), indium metal (Alfa Aesar, 99.99%), and NH₃ (BOC Gases, 99.99%).

B. Reduction reaction

The reactions were carried out in a twin-chamber reactor made of borosilicate glass (Fig. 1). The reactor was charged in an argon-filled glovebox; Chamber B was charged with tantalum halide (approximately 5–10 g of salt for approximately 100 ml of solution), and Chamber A was charged with sodium (in stoichiometric excess by 2 to 20% on a molar basis). The reactor was then removed from the glovebox, connected to a gas train, and flooded with anhydrous ammonia gas for several hours at room temperature. Following this, the reactor was immersed in a cryostat (model FP50-MV, Julabo USA, Kutztown, PA) maintained at –45 °C, which is lower than the normal boiling point of ammonia (–33 °C). Ammonia gas condensed to form a solution of sodium in liquid ammonia in Chamber A and a solution of salt in liquid ammonia in Chamber B. Then, the blue sodium–ammonia solution was poured, in several steps, into the salt–ammonia solution. There was an immediate chemical reaction resulting in the generation of an ultrafine black powder which quickly settled to the bottom of the

TABLE I. Taxonomy of precipitation reactions.

Chemical reaction pathway	Phasality ^a	
	Single phase	Multiphase
Electron transfer (redox)	$\underline{\text{TaCl}_5} + 5 \underline{\text{Na}} \xrightarrow{\text{ammonia}} \text{Ta(s)} + 5 \underline{\text{NaCl}}$	$\underline{\text{K}_2\text{TaF}_7} + 5 \text{Na(l)} \xrightarrow{\text{molten salt}} \text{Ta(s)} + 2 \underline{\text{KF}} + 5 \underline{\text{NaF}}$
Metathesis (exchange)	$\underline{\text{NaCl}} + \underline{\text{AgNO}_3} \xrightarrow{\text{H}_2\text{O}} \text{AgCl(s)} + \underline{\text{NaNO}_3}$	$\underline{\text{NOCl}} + \underline{\text{AgNO}_3(\text{s})} \xrightarrow{\text{N}_2\text{O}_4} \text{AgCl(s)} + \text{N}_2\text{O}_4(\text{l})$

^aThe underline denotes that the species is dissolved in the liquid reaction medium (named above the arrow).

chamber. When the reaction was judged to be complete, the reactor was inverted and the contents of the reaction chamber were filtered. At this time the filtration tube (Chamber C) was wrapped in thermal insulation while the chamber collecting the colorless filtrate (Chamber D) was immersed in the cryostat. Then the temperature of the cryostat was raised slowly. This promoted the evaporation of ammonia from Chamber D which was evacuated to 10^{-2} Pa. On the filter was a mixture of white and black powders; in Chamber D, when all the ammonia had evaporated, white powder remained.

Reasoning that the solubility of tantalum halide in liquid ammonia would increase with the size of the molecule, we used TaBr₅ as the starting material on several occasions. Whereas the bromide was indeed observed to be more soluble than the chloride in liquid ammonia (at -45 °C the solubility of TaCl₅ in liquid ammonia was about 5 g/100 ml and about 12 g/100 ml for TaBr₅), we saw no advantage in using the bromide, and so the majority of syntheses were performed by reduction of the chloride.

C. Ammonia extraction

The reactor was opened in a glovebox under an atmosphere of argon, and there the mixture of powders retained by the filter was charged into a Soxhlet extraction tube. Liquid ammonia was used as the solvent and the extraction continued for over 40 h, after which time all that remained was black powder.

D. Analysis

The powders were characterized by (i) quantitative chemical analysis: tantalum, niobium, aluminum, sodium, and chlorine contents were determined by neutron

activation analysis (SLOWPOKE Nuclear Reactor Facility, University of Toronto), while nitrogen and oxygen contents were measured by inert gas fusion (model TC-436 nitrogen/oxygen determinator, LECO Corp., St. Joseph, MI); (ii) x-ray diffraction (XRD; model D/max-3c, Rigaku Inc., Danvers, MA); and (iii) scanning transmission electron microscopy (TEM; model VG-HB603, Vacuum Generators, Hastings, UK).

III. RESULTS

A. Synthesis and characterization of tantalum powder

The black powder taken from the Soxhlet extraction tube was very fine. Particle size was determined by TEM. Samples were prepared in the glovebox where the TEM grate was immersed in the powder, raised gently, and finally packed in a bottle secured by an O-ring seal. The bottle was removed from the glovebox. Just before analysis by TEM the bottle was opened, the grate extracted and loaded onto a sample holder, and quickly transferred to the TEM sample chamber. The primary particle size was estimated to be in the range of 20 to 60 nm [Fig. 2(a)], which is over an order of magnitude finer than commercial powder; in addition, the particles appeared to be somewhat porous [Fig. 2(b)]. Chemical analysis (Table II) suggests that this material is metallic tantalum along with some impurities. Accordingly, we conclude that the reaction of sodium with TaCl₅ proceeds according to Eq. (2); if parasitic ammonolysis occurs, its extent is only slight as evidenced by the relatively small concentrations of nitrogen and hydrogen, which can be explained by retention of extraction solvent. Furthermore, the nitrogen content of the powder is far too low for tantalum amide. The oxygen level is an indication of the powder's high reactivity with air and water, the reactivity dependent upon the ratio of reductant to salt. Specifically, the powder made with a high ratio of sodium to salt ($5\text{Na}:\text{TaCl}_5 > 1.2$) is very active: This material catches fire upon exposure to air and is active even in an Ar-filled glovebox. The powder made with a low reducing agent ratio ($5\text{Na}:\text{TaCl}_5 < 1.1$) also reacted with air but the reaction progressed more slowly, taking several hours to convert the black metallic powder to oxide. The differences in reactivity are not attributed to differences in particle size but rather to the presence of entrained, unreacted sodium. In the course of LECO combustion analysis there is brief exposure to the air that could account for the oxygen level measured in this specimen. The presence of sodium and chlorine is presumed to be the result of incomplete removal of sodium chloride as evidenced by the observation that the refluxing causes the sodium and chlorine levels in the powder product to decrease. In parallel, the

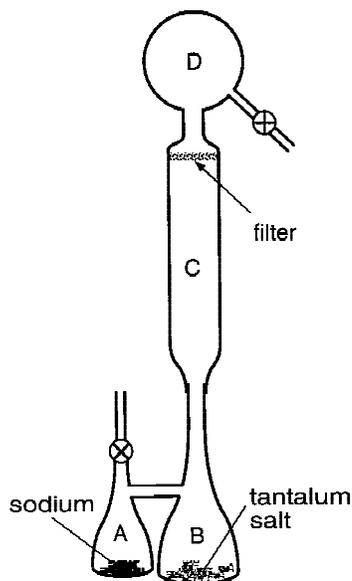
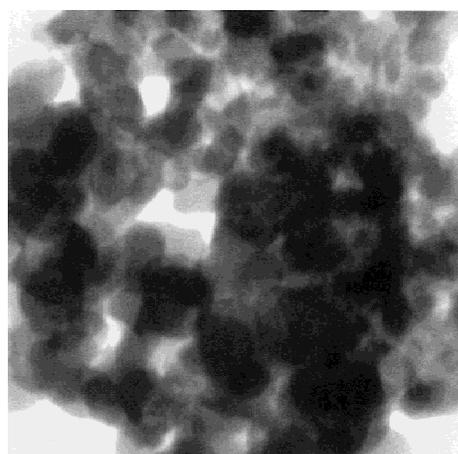


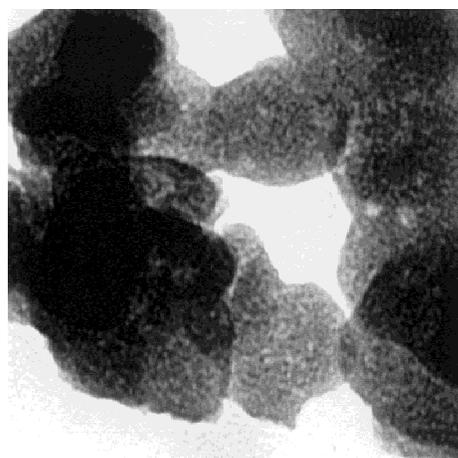
FIG. 1. Pyrex reactor.

presence of sodium chloride in the filtrate solution was confirmed by XRD of the material left after evaporation of same (Fig. 3).

Figure 4 shows the XRD results for the black powder after ammonia extraction. With two broad peaks at around $2\theta = 33^\circ$ and 56° , this is not the pattern representative of crystalline, elemental body-centered cubic tantalum for which the reflections are calculated to be at $2\theta = 38^\circ$, 56° , and 70° . Peak broadening is characteristic of atomic disorder. Further evidence of this is found in the diffuse halo in the electron diffraction image shown in Fig. 5. We conclude that the powder is either amorphous or nanocrystalline.



(a) 100 nm



(b) 40 nm

FIG. 2. Scanning TEM images of tantalum powder.

TABLE II. Quantitative analysis of tantalum powder after ammonia extraction.

Elements	Ta	O	N	H	Na	Cl
wt%	90	3.3	3.9	1.3	1.1	2.0

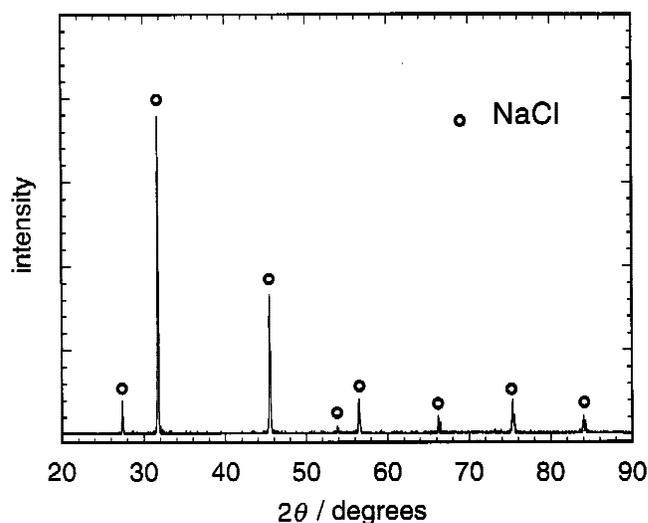


FIG. 3. XRD pattern of filtrate.

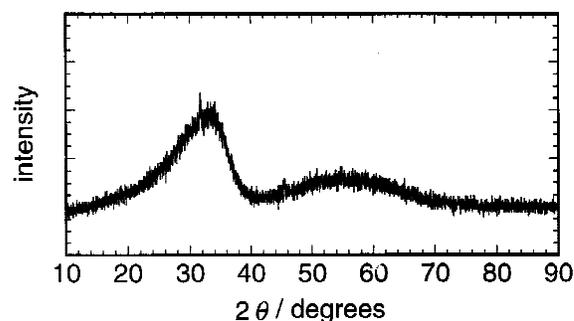


FIG. 4. XRD pattern of tantalum powder.

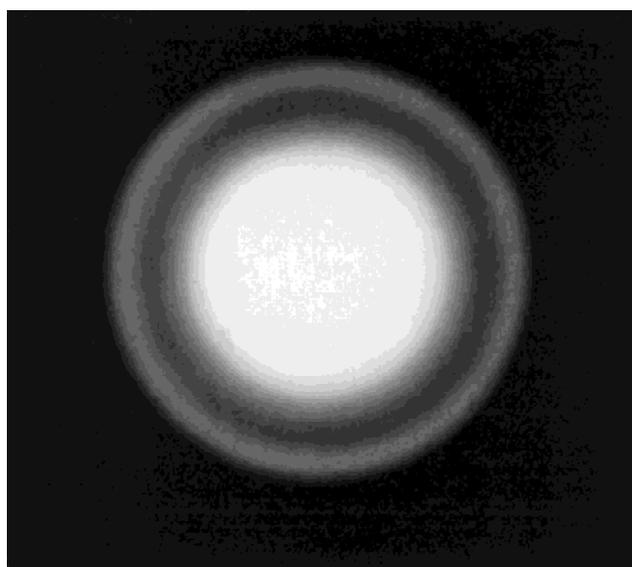


FIG. 5. Electron-diffraction pattern of tantalum powder.

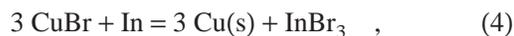
B. Synthesis and characterization of copper powder

To verify that the substantial reduction in particle size of the tantalum powder was due to the electronic conductivity of liquid ammonia and not simply the difference in temperature between liquid ammonia (−40 °C versus 850 °C), we investigated the production of copper powder by electronically mediated reactions in two different media. One allowed electronic conduction; the other did not.

The homogeneous reaction, conducted in liquid ammonia at −40 °C, is



where the underline denotes dissolution in liquid ammonia. The heterogeneous reaction, conducted in water at 20 °C, is

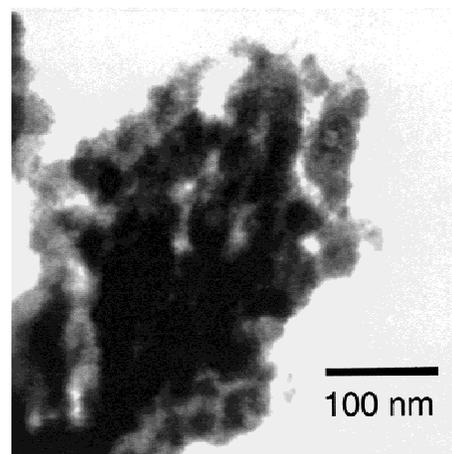


where the underline denotes dissolution in water. The copper powder produced by Reaction (3) had an average particle size of approximately 10 nm and was x-ray amorphous. The powder produced by Reaction (4) had an average particle size of approximately 100 nm and was crystalline. Because these results for copper so closely mimic those for tantalum, we believe that the observed changes in particle size are more the result of changes in the electrical properties of the reaction medium than changes in reaction temperature.

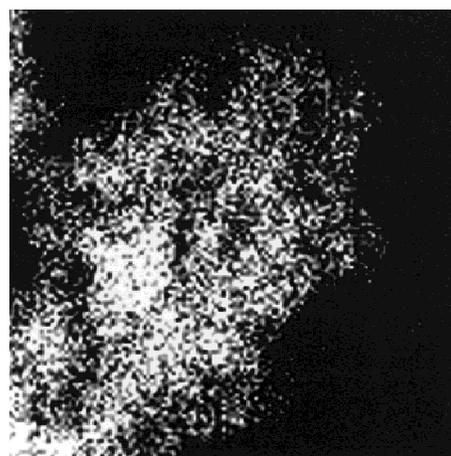
C. Synthesis and characterization of Nb₃Al powder

Because the reaction of metal halides and alkali metal in the ammonia solution is homogeneous, we reasoned that production of nanosized particles of multiple elements should be possible. To verify this, we attempted the synthesis of niobium aluminide, Nb₃Al. Following the experimental procedure described in Sec. II. B for the generation of tantalum powder, both NbCl₅ and AlCl₃ were dissolved in liquid ammonia in the molar ratio of NbCl₅:AlCl₃ = 3 (approximately 5–10 g of salt in 100 ml of solvent). This was reacted with a solution of sodium dissolved in liquid ammonia (sodium in stoichiometric excess by approximately 10% on a molar basis). Product powder was annealed at 500 °C in vacuum for 2 h.

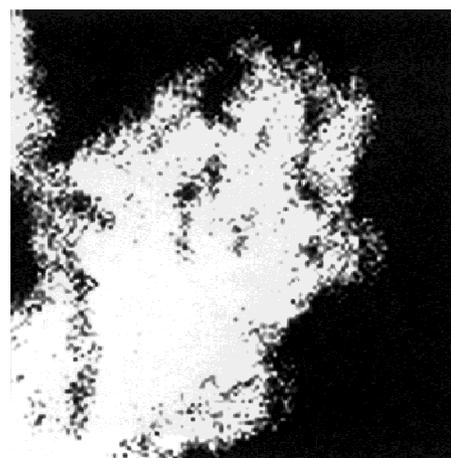
Figure 6(a) shows a scanning transmission electron micrograph of the powder after rinsing with liquid ammonia. Figures 6(b) and 6(c) show the same region of the material subjected to energy-dispersive x-ray analysis. It is evident that the powder consists of niobium and aluminum distributed throughout. In other words, we have not made islands of aluminum and niobium—the two elements are well mixed. By neutron activation analysis the Nb:Al ratio was measured to be 3:1. We conclude



(a)



(b)



(c)

FIG. 6. (a) Scanning TEM image of niobium aluminide powder. (b) Energy-dispersive x-ray analysis of niobium aluminum powder: Nb dot map. (c) Energy-dispersive x-ray analysis of niobium aluminum powder: Al dot map.

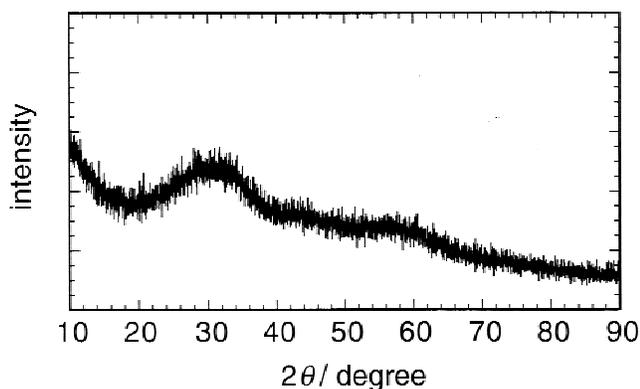


FIG. 7. XRD pattern of niobium aluminide powder.

that the powder is Nb₃Al. Figure 7 shows the XRD pattern of this material. As was the case with the tantalum powder, we observed broad peaks and judge the powder to be x-ray amorphous.

The synthesis of niobium aluminide is interesting on thermodynamic grounds. We have shown that in liquid ammonia TaCl₅ will react with sodium to produce elemental tantalum. Therefore, it is to be expected that NbCl₅ will do the same. In contrast, when we attempted the analogous reaction with AlCl₃, no metal was produced even though the reaction to form elemental aluminum and sodium chloride is energetically favored. We assume that the reaction to make elemental aluminum is superseded by ammonolysis in agreement with earlier observations with AlI₃.⁵ Furthermore, when the mixed NbCl₅-AlCl₃ solution was reacted with sodium, the amount of chlorine present as NaCl in the filtrate exceeded the amount of chlorine available as NbCl₅. The scanning TEM analysis confirms that aluminum is present in the product powder. Perhaps by forming the intermetallic compound the chemical potential of Al is reduced to the point where ammonolysis is suppressed.

IV. CONCLUSIONS

The analysis of metallothermic reduction as an electronically mediated reaction predicted that particle size could be reduced if the reaction were conducted in a medium that is a mixed conductor (ionic and electronic). This prediction has been confirmed by the present investigation in which tantalum powder was produced with an average particle size more than an order of magnitude finer than the micron-sized powders produced commercially today. The powder is amorphous in both x-ray and scanning TEM analyses. To show that this is not simply

a temperature effect, copper precipitation from media with different electrical properties was examined at nearly equal temperatures. Results comparable to those for tantalum were obtained. As for the possibility that the observed change in particle size is attributable to the presence of impurities, our nanosized powders are generated by homogeneous nucleation from a liquid in which all reactants have been dissolved. To have an impact on the final particle size under these circumstances, then, the impurities would have to dramatically alter the surface energy of the product or of the saturated ammonia solution which, in turn, would affect the value of the critical radius for nucleation. The impurities reported in Table II are not known to be surface active in tantalum, and the size of powder produced in liquid ammonia far exceeds the critical radius; thus, we judge the presence of impurities not to have had a significant influence on particle size in our experiments. Last, metallothermic reduction in a mixed conducting medium has been extended to a multicomponent system with our demonstration of the synthesis of nanosized powder of Nb₃Al by co-reduction of NbCl₅ and AlCl₃. Perhaps forming the intermetallic compound reduces the chemical potential of Al to the point where ammonolysis is suppressed.

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