

MATERIALS SYNTHESIS BY METALLOTHERMIC REDUCTION

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ABSTRACT

For many years metallothermal reduction has been used in the primary extraction of metals. Recent work in this laboratory has found the commonly held view that metallothermal reduction is strictly a chemical reaction and that the process is rate limited by mass transfer to be incomplete. In a study of the production of tantalum powder by the reaction of K_2TaF_7 with sodium in a molten salt medium at $850^\circ C$, it has been shown that there are two dominant kinetic pathways, both involving electron transfer. Furthermore, the overall rate of reaction is limited by electron transport between the reactants. Hence, we have dubbed metallothermal reduction an “electronically mediated reaction” (EMR). The location of the tantalum deposit and its morphology are both governed by the reaction pathway. With knowledge of the EMR concept, a parallel set of experiments was conducted in which tantalum powder was produced by the reaction of $TaCl_5$ with sodium, both dissolved in liquid ammonia at $-35^\circ C$. Nanosized powder of high purity was obtained. The concept has been extended to include the synthesis of intermetallic compounds in liquid ammonia by co-precipitation of multiple elements. Nanosized powder of Nb_3Al was produced by the co-reduction of $NbCl_5$ and $AlCl_3$ with sodium dissolved in liquid ammonia.

INTRODUCTION

Tantalum is produced by metallothermal reduction of one of its salts [1,2]. At approximately $800^\circ C$, solid potassium heptafluorotantalate (K_2TaF_7) and liquid sodium are added to a halide melt (known as a “diluent”) where they react to produce solid tantalum in the form of powder. The central reaction for this process is



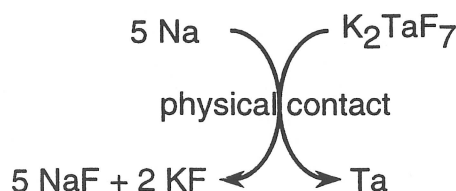
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where the underline denotes that the species is dissolved in the diluent. This process is representative of a set of primary extraction technologies that produce metal by reaction of one of its compounds with a metallic reducing agent. Magnesium, titanium, zirconium, beryllium, neodymium, and tantalum are all examples of metals produced by metallothermic reduction.

The commonly held view is that metallothermic reduction is strictly a chemical reaction and that the process is rate limited by mass transfer. The study of tantalum production by Eq. 1 has shown that the reaction mechanism of metallothermic reduction includes electron-transfer steps, and furthermore, that it is the rate at which electrons produced by the anodic steps are transported to the cathodic steps that controls the overall rate of reaction. For this reason, we have termed metallothermic reduction to be an “electronically mediated reaction” (EMR). In addition, there is evidence that the mode of electron transport between reactants influences the morphology of the metal product. Recognition of the role of electron transport has important consequences for process design and optimization.

The importance of electron transport inspired a second part to this study, namely a parallel set of experiments conducted in liquid ammonia. In contrast to the molten salt diluent, which dissolves K_2TaF_7 but not sodium (feed but not reductant), liquid ammonia dissolves *both* sodium as well as a number of tantalum salts, *e.g.*, $TaCl_5$ (feed *and* reductant). The sharp contrast between the electrical properties of the molten salt medium, which is predominantly an ionic conductor, and liquid ammonia, which solvates electrons, provided the backdrop for a critical assessment of the EMR concept.

(a) Metallothermic Reduction (MR)



(b) Electronically Mediated Reaction (EMR)

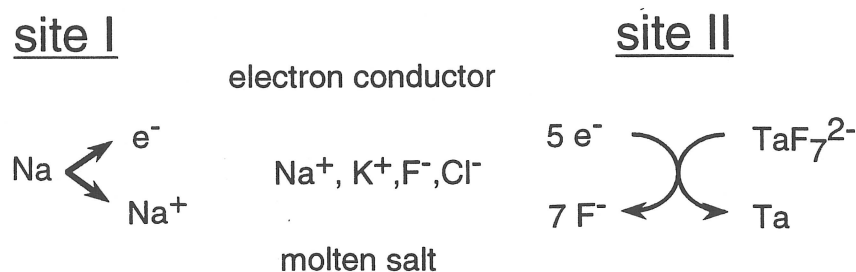


Figure 1. Schematic of two reaction pathways for metallothermic reduction.

- (a) mixing of reactants -- direct physical contact;
- (b) electronic mediation -- no contact between reactants

METALLOTHERMIC REDUCTION AS AN ELECTRONICALLY MEDIATED REACTION

Conventional metallothermal reduction is based on direct physical contact between feed (compound to be reduced) and reductant (metallic reducing agent), schematically illustrated in Figure 1(a). Mixing of feed and reductant is achieved by mass transport through the reaction medium. As a complement to this conventional view of metallothermal reduction, we proposed that metallothermal reduction necessarily includes electron transport, *i.e.*, the mechanism of Eq. 1 includes electron-transfer steps together with the transport of electrons between reactants. For example, Eq. 1 can be expressed as the sum of the following two partial reactions, each of which involves electron transfer:



Strictly speaking, the reaction represented in Eq. 2 likely proceeds in multiple steps, *e.g.*, 5+ to 4+, *etc.* [3-11], but such details do not detract from the conclusions of this study. What is missing from equations 2 and 3 is the explicit statement of the requirement of electron transport from sodium (reductant) to K_2TaF_7 (feed). The fact that the molten halides typically employed as diluents are extremely poor conductors of electrons leads one to expect that the rate of tantalum production is controlled not simply by mass transfer of K_2TaF_7 and sodium, but rather by the rate of electron transport from sodium to tantalum. Hence, the overall reaction can be viewed as an *electronically mediated reaction (EMR)*. This is shown schematically in Figure 1(b).

When EMR is operative, the reactor can be viewed as functioning much like a primary battery: the reductant acts as the anode or electron source, the diluent acts as the electrolyte, and the metal product acts as the cathode or electron sink. A metallic object that contacts both sodium and K_2TaF_7 functions as the “load” in such a battery circuit and provides a low-resistance path for the electrons.

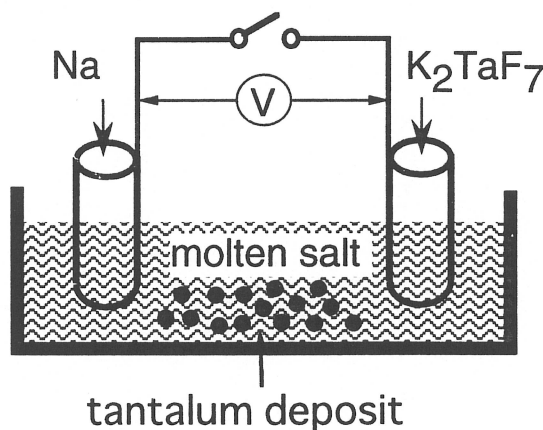
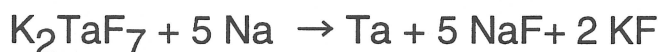
It is further hypothesized that there are two types of EMR: “short-range” and “long-range.” Short-range EMR (SREMR) occurs by electron transfer through the molten salt medium and is effectively identical to the conventional model of metallothermal reduction as a thermochemical reaction. In contrast, long-range EMR (LREMR) does not involve direct physical contact between feed and reductant. Instead, the reaction occurs by electron transfer through an electronically conductive medium, *e.g.*, reactor wall, stirrer, or even the tantalum deposit itself.

EXPERIMENTAL DESIGN

To test the hypothesis that metallothermal reduction occurs by electrochemical steps in which the kinetics are controlled by electron transport between reactants and to demonstrate the existence of LREMR, experiments were conducted according to the schematics shown in Figure 2. Figure 2(a) shows metallothermal reduction by SREMR, *i.e.*, K_2TaF_7 and sodium are introduced via open ended drop tubes into the diluent where they react only after making physical contact. The diluent is a multicomponent halide melt

containing sodium ions. Figure 2(b) shows almost the same setup as Figure 2(a) but with one exception. The drop tubes containing K_2TaF_7 and sodium are electrically connected through an external circuit. This allows the reactions described by Equations 2 and 3 to proceed without physical contact between K_2TaF_7 and sodium. Electrons produced upon the formation of sodium ions according to Eq. 3 need not be donated directly to a contacting tantalum ion but instead can travel along the external conductor to the compartment containing K_2TaF_7 . In this case electrons produced by the ionization of sodium in the left chamber are transported through an external circuit to the fluorotantalate ions (TaF_7^{2-}) in the right chamber. There, they can reduce tantalum ions to metal. If such LREMR exists it should be manifest in the form of a current flowing in the external circuit. Furthermore, if LREMR is operative we should expect the production of tantalum powder to be confined to the right chamber where fluorotantalate is reduced due to the injection of electrons from the external circuit. LREMR is generally overlooked in the analysis of metallothermic reduction operations although it can be operative, if not dominant, in many instances.

(a) Metallothermic Reduction, or Short-Range-EMR



(b) Electronically Mediated Reacton, or Long-Range-EMR

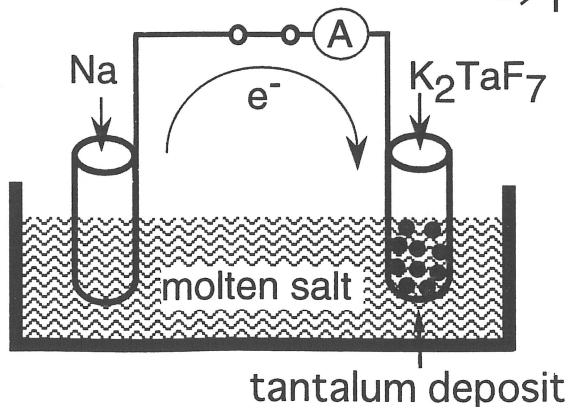
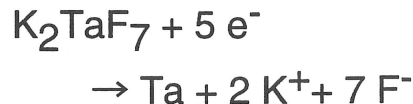


Figure 2. Design of experiment to prove the existence of long-range EMR.

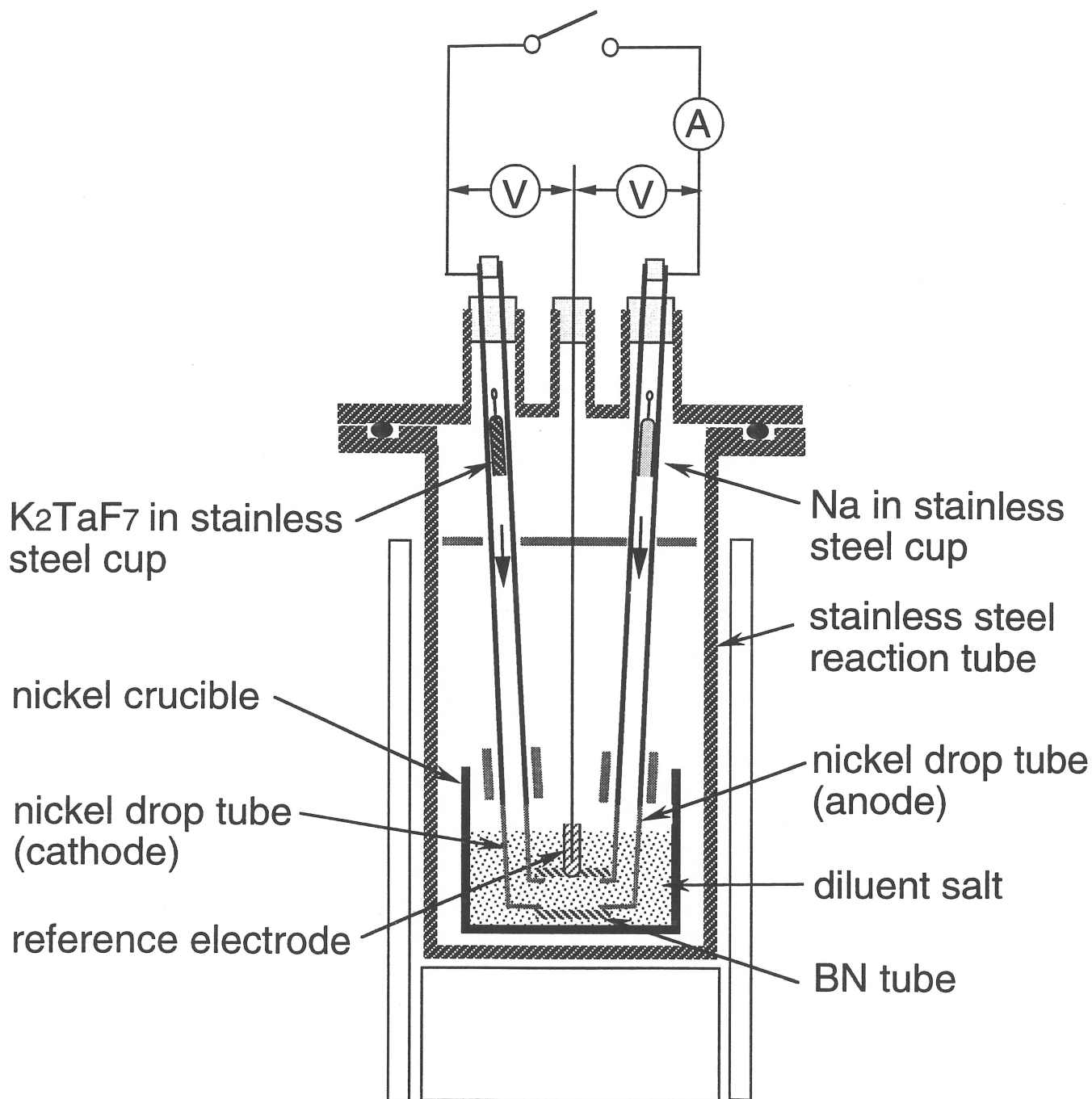


Figure 3. Experimental apparatus.

Figure 3 shows the experimental apparatus. The nickel drop tubes for the samples, boron nitride spacer, thermocouple sheath (not shown in the figure), two identical reference electrodes (only one shown in the figure), and the diluent salt were placed in the nickel crucible which measured 7.6 cm O.D. The reference electrode was a closed-one-end tube made of hot-pressed boron nitride. Inside was a nickel wire immersed in a melt consisting of the diluent salt to which NiF_2 was added to the level of 1 mol %. The bottom of the BN tube was milled down to a thickness of less than 1 mm to allow rapid establishment of electrical contact between the diluent salt and the melt in the reference electrode. About 440 g of diluent salt was charged into the nickel crucible. Prior to the experiment, K_2TaF_7 feed (mass 24.2 g) and sodium reductant (mass 12.8 g, which exceeds the stoichiometric

amount required by Eq. 1) were cast under argon atmosphere (grade 5.0, 1 ppm oxygen) into stainless steel cups. These cups were positioned at the top of the nickel drop tubes. The reaction tube was then assembled, evacuated to a pressure of 1 kPa, and heated to 400°C for 12 hours to remove moisture. The cell was back filled with argon, and the temperature was increased to 800°C. Once the diluent salt had melted, the reference electrodes were immersed into the diluent, and the external circuit was shorted. In some experiments, potassium was used as reductant. In such instances, the reaction temperature was reduced to 700°C to avoid boiling of the potassium metal.

The experiment began by dropping the cups containing the reductant and feed. Current was monitored in the external circuit by measuring voltage across a 1 m Ω standard resistor acting as a shunt. The data were taken by voltmeter (Keithley Model 181 Nanovoltmeter) and digital multimeter with eight-channel scanner (Keithley Model 199) and logged onto a PC via GPIB interface using software written in house. When the current in the external circuit dropped to below 0.5 A (typically this took about 2 hours) the experiment was terminated. The reference electrodes and the thermocouple were raised out of the diluent melt, and the power to the furnace was cut. The cell and its contents furnace-cooled to room temperature. Samples were taken of the solidified diluent and tantalum metal product. In total, about 10 g of tantalum was produced in a typical experiment. Metal powder was found throughout the channel formed by the nickel drop tubes and the boron nitride connector. Samples of this material were analyzed by x-ray diffraction and electron probe microanalysis.

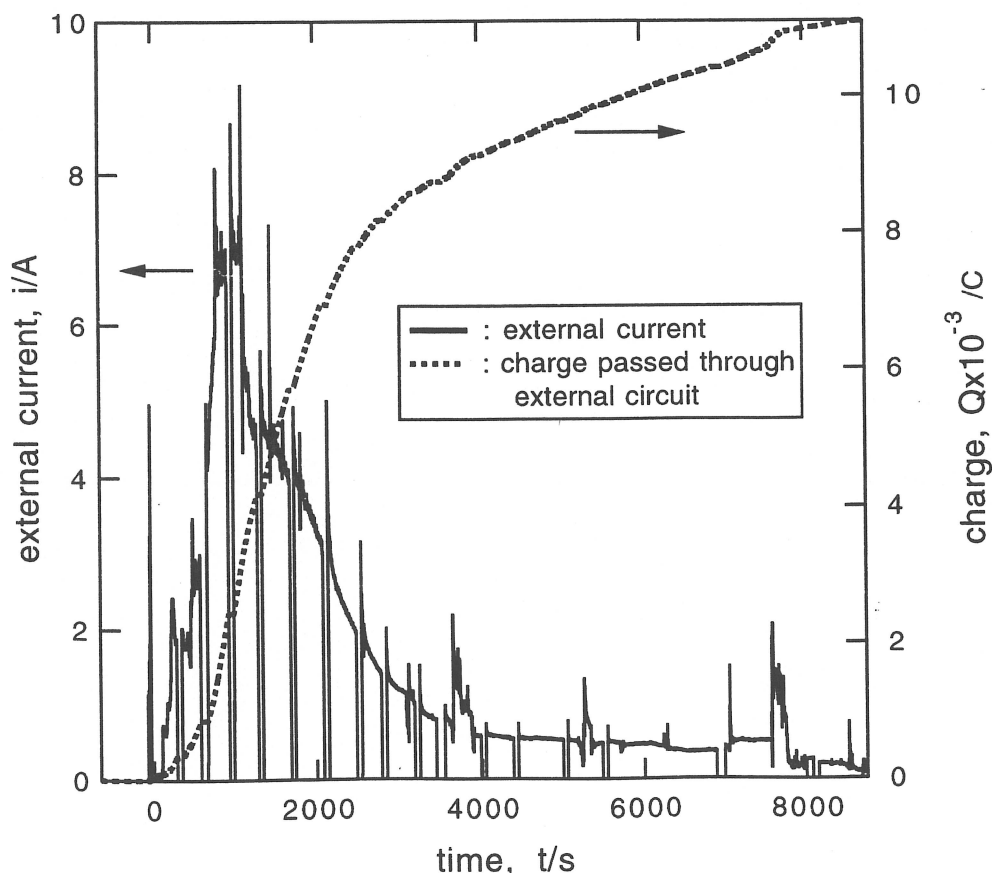


Figure 4. Measured current in the external circuit. Current spikes caused by occasional interruption of current to measure open-circuit potentials.

RESULTS

Figure 4 shows the current *versus* time trace for a representative experiment. Time zero is measured from the moment the feed and reductant were dropped into the diluent. Over the first 15 minutes the current rose steadily, reaching a maximum value of almost 8 A, and then decreasing over the next hour to below 1 A. The current spikes seen in the figure are experimental artifacts caused by occasional interruption of external current to allow measurement of the open-circuit potentials between the reference electrode and each drop tube. At the time of maximum current an open-circuit potential of 0.9 V was measured between the two drop tubes. The total electrical charge passed through the external circuit was calculated by evaluating the time integral of the current shown in Figure 4 and found to be 11100 C.

Clearly, the presence of current in the external circuit proves the existence of LREM — since feed and reductant are physically separated there is no way for the reaction to proceed by SREM. It takes 29800 C or 0.3085 moles of electrons to reduce completely 24.2 g of K_2TaF_7 (Ta^{5+}) to metallic tantalum (Ta^0). During the course of our experiment 11100 C passed through the external circuit. Therefore, at least 37% of the tantalum is produced by LREM, *i.e.*, without any direct physical contact between the K_2TaF_7 feed and the sodium reductant. In other words, it is the action of electrons donated by the sodium reductant to the electronically conductive medium in contact with both the sodium and the K_2TaF_7 feed that produces tantalum.

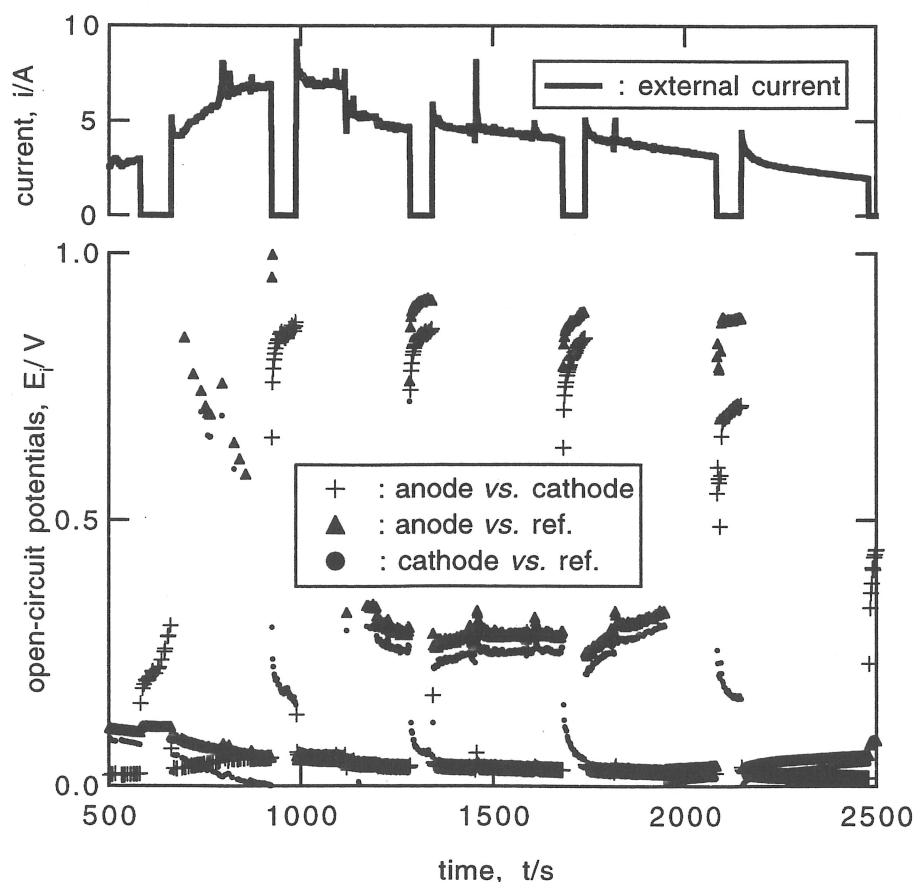


Figure 5. Measured open circuit potentials.

Figure 5 shows the variation of open circuit potentials during the course of an experiment. Periodically the current in the external circuit was interrupted, and voltages were measured (i) between the Ni/Ni²⁺ reference electrode and the K₂TaF₇ feed tube and (ii) between the Ni/Ni²⁺ reference electrode and the molten sodium. In the terminology of batteries, the K₂TaF₇ is acting as the cathode, while the sodium is acting as the anode. The driving force for the reaction between them was measured to be approximately 0.8 V. The Nernst potential calculated from the reported Gibbs free energy of formation of K₂TaF₇ is 1.4 V [12, 13]. Also, voltammetry in CsCl-KCl-NaCl-K₂TaF₇ melts shows a one-step reduction of Ta⁵⁺ to metal at a half-wave potential of 0.9 V *versus* Ag/AgCl. Given the expected electronic shorting caused by the high volatility of the metal reductant and possible degradation of the reference electrode in such a strongly reducing environment the measurement of somewhat lower voltages is judged to be reasonable under the circumstances.

Table I. Some representative conditions and results for metallothermic reduction of K₂TaF₇ by LREMR at 1073 K.

expt. no.	amount of reactant		temp. (°C)	reaction time (s)	observed current		charge through external circuit (C)	Ta fraction produced* by LREMR
	K ₂ TaF ₇ (g)	reductant (g)			max. (A)	average (A)		
1	39.1	12.6	800	14000	7	0.87	12200	25%
2	24.2	12.8	800	8600	8	1.29	11100	37%
3	16.4	12.2	700	3700	3	0.84	3100	15%
4	9.26	9.65 ⁺	700	4800	3	0.91	4400	38%

* percentage of K₂TaF₇ reduced by LREMR is calculated from the ratio of charge transported through the external circuit to total charge required to reduce all tantalum present in the feed

+ potassium was used as reductant.

Representative results of experiments demonstrating the existence of LREMR are summarized in Table I. In all cases, substantial currents were measured in the external circuit. By comparing the quantity of charge that passed through the external circuit to the total charge that would be required to fully react with the K₂TaF₇ reactant, the fraction of K₂TaF₇ that was reduced by LREMR was calculated. The results indicate that the extent of LREMR is not insignificant; in some experiments, almost 40% of the tantalum was produced by LREMR. The poor reproducibility may be attributed to leakage currents, which can be traced to the high vapor pressure of the metal reductant at the temperature of the experiment. This can also explain the surprisingly large fraction of tantalum produced by LREMR in experiment 4 when potassium, rather than sodium, was used as the reductant. Potassium was expected to be more soluble than sodium in the molten salt diluent with the result that the electronic conductivity is higher. This should increase the likelihood of SREMR, an expectation that was not supported by experimental evidence. Even with potassium as the reductant, the extent of LREMR was substantial.

In all cases, tantalum metal was found in the cathode tube and at the bottom of the crucible. Figure 6 shows how the morphology of the metal product is affected by the mechanism of the reduction reaction. Figure 6(a) shows fine, unagglomerated tantalum powder harvested

from the bottom of the crucible. This material is presumed to have formed by homogeneous nucleation in the diluent melt, which implies SREMR. Figure 6(b) shows the tantalum produced inside the fluorotantalate drop tube. This material is not loose powder but rather a compact deposit adhering to the metallic substrate. This is what one would expect for a metal produced by LREMR, which involves electron transport via a conducting intermediary substrate on which heterogeneous nucleation of tantalum metal occurs. These results indicate that two rather different types of metal product are formed depending upon the kinetic pathway.

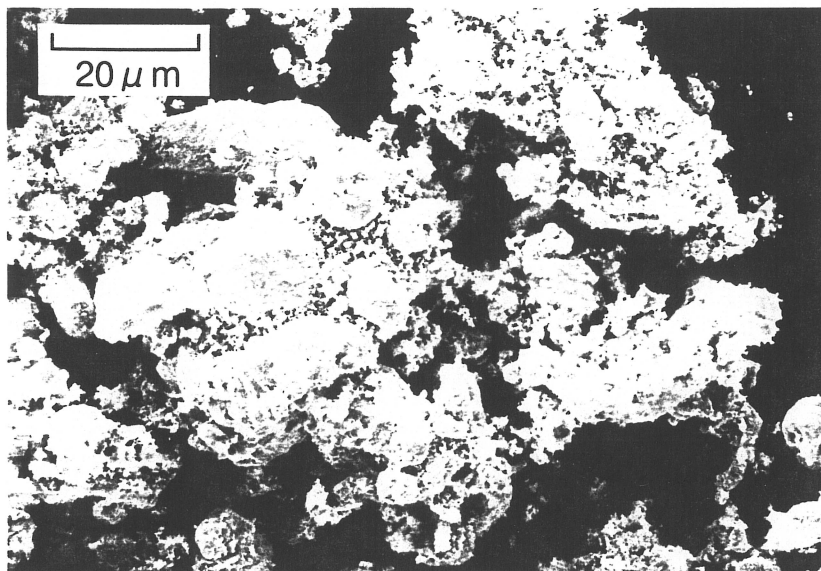


Figure 6. (a) Tantalum powder obtained from bottom of reactor vessel.

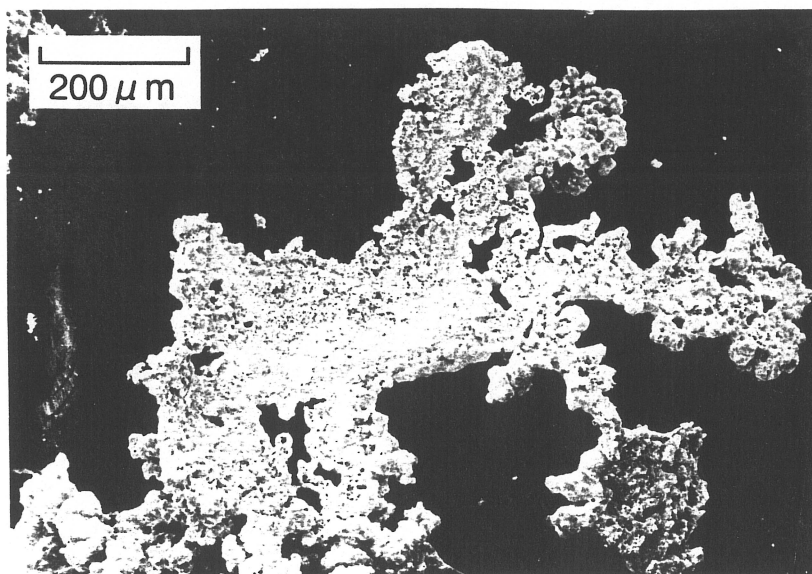


Figure 6. (b) Tantalum powder obtained in the cathode tube.

DISCUSSION

Industrial practice provides more evidence. In the Kroll process, titanium tetrachloride is reacted with magnesium to produce titanium metal in the form of sponge [14]. Because magnesium is almost insoluble in multicomponent melts containing magnesium chloride [15], there is effectively no electronic conduction in the melt [16]. Hence, the dominant kinetic pathway is LREM and the product metal is in the form of a dense, compact deposit known as sponge. In the Hunter process, titanium tetrachloride is reacted with sodium [17]. Here, titanium metal is produced mainly in powder form. At elevated temperatures sodium is quite soluble in sodium chloride [18]. Sodium dissolution is accompanied by electron solvation which enhances SREM and, hence, powder formation. Thus, it seems that the difference in the morphologies of Kroll and Hunter titanium can be explained by the difference in the electrical properties of the molten salt reaction media.

Table II: Recommended operating practices to tailor the characteristics of metal produced by metallothermic reduction

* powder *	* dense, compact metal *
☞ enhance SREM	☞ enhance LREM
1. mixing	1. no mixing
2. minimize the use of metal components	2. maximize surface area of electronically conductive medium
3. polarize metal anodically	3. polarize metal cathodically
4. charge with excess reductant, <i>i.e.</i> , in excess of feed	4. charge with excess feed, <i>i.e.</i> , in excess of reductant
5. render diluent electronically conductive	5. render diluent ionically conductive
6. mix feed and reductant in the charge	6. charge feed and reductant remotely

The results of this study can be generalized to other metallothermic reduction processes, to change either product morphology or process chemistry. Table II shows how to exercise morphological control over the product. For example, to make a dense, compact metal product requires that one take steps to ensure that LREM is the dominant kinetic pathway in order to enhance heterogeneous nucleation of new metal on selected substrates while repressing homogeneous nucleation of powders in the bulk of the diluent medium. In parallel, the level of electronic conduction should be kept at a minimum in the diluent salt. Practical measures include charging feed and reductant at different locations in the reactor and avoiding mixing. To minimize electronic conduction, feed should be charged in stoichiometric excess of reductant. Lastly, LREM can be further enhanced by cathodic polarization of the substrate on which metal product is forming.

Process chemistry can also be affected thanks to an understanding of the role of EMR in metallothermic reduction. Specifically, recognition of the effects of LREM opens up new possibilities in the choice of reductant. This is due to the fact that LREM occurs without direct contact between feed and reductant, thereby avoiding the undesirable effects of contamination of the metal product by impurities that may be present in the reductant. For example, one can imagine a process in which titanium tetrachloride is reacted with

magnesium scrap to produce titanium metal. If the reaction is controlled so as to proceed strictly by LREM (this can be managed by reactor design), the reductant can be physically separated from the feed and thus there is no danger of contaminating the product metal with impurities and alloying elements present in the magnesium scrap. Using magnesium scrap instead of high-purity magnesium or sodium as the reductant offers significant cost advantages and is at the same time environmentally friendlier than the present technology. In the absence of an understanding of LREM, use of magnesium scrap in this application would be unthinkable. In other words, the old adage of process metallurgy has been overturned. Previously it was thought that to make high-purity product required high-purity feed *and* high-purity reductant. Understanding LREM points the way to processes in which it may be possible to make high-purity product from high-purity feed and *low-purity* reductant. Verification awaits further research.

SYNTHESIS OF INTERMETALLIC COMPOUNDS BY REDUCTION OF MULTICOMPONENT SOLUTIONS OF LIQUID AMMONIA

Ammonia dissolves alkali metals. For example, sodium will dissolve in liquid ammonia to give Na^+ and a solvated electron. The result is a medium that is very potent for chemical reactions involving metallothermic reduction where it is known that the slow step is not mass transport, *i.e.*, transport of reagents, but rather, electron transport, *vide supra* [19]. We have investigated whether it is possible to make tantalum powder by reacting a solution of TaCl_5 dissolved in liquid ammonia with a solution of Na dissolved in liquid ammonia. While in the absolute, sodium should reduce TaCl_5 , in the presence of liquid ammonia there is the possibility that instead of tantalum metal, the product of reaction is some tantalum amine compound. Our study has shown that indeed tantalum metal forms. The advantage of this process is that because the temperature of reaction is -40°C , the particle size of the tantalum powder is much finer than that produced by conventional technology which operates at much higher temperatures (near 850°C). We have made powder that averages 20 nm in diameter, far less than the micron-sized material produced by the industrial process.

Beyond this, we have tried co-precipitation/co-reduction of metals by first dissolving multiple compounds of the metals in liquid ammonia and then reducing the solution to promote the precipitation of a heteronuclear compound product. For example, both NbCl_5 and AlCl_3 were dissolved in liquid ammonia. To this solution of the two salts a solution of Na dissolved in liquid ammonia was added. The sodium reacted with the binary salt solution to produce a dispersion of fine powder, which appears to be the intermetallic compound of niobium and aluminum, Nb_3Al . Why do we believe this to be so? It is known that AlCl_3 is not reduced by Na metal dissolved in ammonia. However, in our experiment with the solution containing *both* NbCl_5 and AlCl_3 , the mass balance on the NaCl product indicates that there is more chlorine present in NaCl than could be obtained from reducing all the NbCl_5 . This means that some AlCl_3 must have been reduced. One explanation is that by forming the compound the chemical potential of Al is reduced to the point where it becomes viable to produce it by reduction of AlCl_3 . Put another way, it is only through compound formation that Al reduction is possible.

Can we imagine other compounds that can be produced in the same manner? Yes, TiB_2 and GaN are two examples.

CONCLUSIONS

The production of tantalum powder by the reaction of K_2TaF_7 with sodium has been studied, and two dominant kinetic pathways, both involving electron transfer, have been found. Electron transport between reactants can be rate limiting; hence, the reaction is considered to be electronically mediated. The location of the tantalum deposit and its morphology seem to depend on the reaction pathway. Recognition that metathallotermic reduction is electronically mediated is helpful for the design of new processes and optimization of existing processes. It would be interesting to test on a wider basis the concepts set forth in the present article; specifically, analysis of other metathallotermic reduction processes within the framework of electronic mediation could prove insightful.

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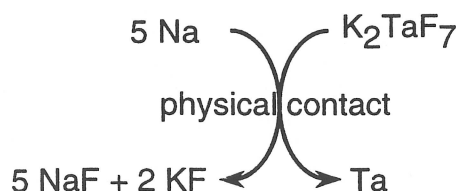
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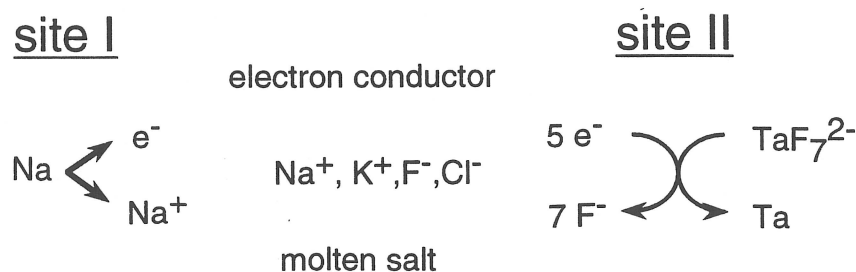


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METALLOTHERMIC REDUCTION AS AN ELECTRONICALLY MEDIATED REACTION

Conventional metallothermal reduction is based on direct physical contact between feed (compound to be reduced) and reductant (metallic reducing agent), schematically illustrated in Figure 1(a). Mixing of feed and reductant is achieved by mass transport through the reaction medium. As a complement to this conventional view of metallothermal reduction, we proposed that metallothermal reduction necessarily includes electron transport, *i.e.*, the mechanism of Eq. 1 includes electron-transfer steps together with the transport of electrons between reactants. For example, Eq. 1 can be expressed as the sum of the following two partial reactions, each of which involves electron transfer:



Strictly speaking, the reaction represented in Eq. 2 likely proceeds in multiple steps, *e.g.*, 5+ to 4+, *etc.* [3-11], but such details do not detract from the conclusions of this study. What is missing from equations 2 and 3 is the explicit statement of the requirement of electron transport from sodium (reductant) to K_2TaF_7 (feed). The fact that the molten halides typically employed as diluents are extremely poor conductors of electrons leads one to expect that the rate of tantalum production is controlled not simply by mass transfer of K_2TaF_7 and sodium, but rather by the rate of electron transport from sodium to tantalum. Hence, the overall reaction can be viewed as an *electronically mediated reaction (EMR)*. This is shown schematically in Figure 1(b).

When EMR is operative, the reactor can be viewed as functioning much like a primary battery: the reductant acts as the anode or electron source, the diluent acts as the electrolyte, and the metal product acts as the cathode or electron sink. A metallic object that contacts both sodium and K_2TaF_7 functions as the “load” in such a battery circuit and provides a low-resistance path for the electrons.

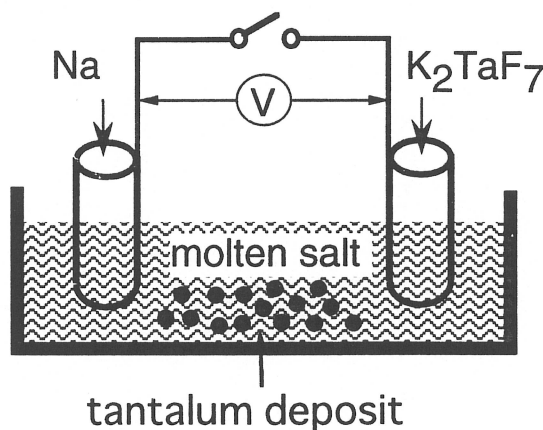
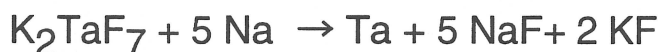
It is further hypothesized that there are two types of EMR: “short-range” and “long-range.” Short-range EMR (SREMR) occurs by electron transfer through the molten salt medium and is effectively identical to the conventional model of metallothermal reduction as a thermochemical reaction. In contrast, long-range EMR (LREMR) does not involve direct physical contact between feed and reductant. Instead, the reaction occurs by electron transfer through an electronically conductive medium, *e.g.*, reactor wall, stirrer, or even the tantalum deposit itself.

EXPERIMENTAL DESIGN

To test the hypothesis that metallothermal reduction occurs by electrochemical steps in which the kinetics are controlled by electron transport between reactants and to demonstrate the existence of LREMR, experiments were conducted according to the schematics shown in Figure 2. Figure 2(a) shows metallothermal reduction by SREMR, *i.e.*, K_2TaF_7 and sodium are introduced via open ended drop tubes into the diluent where they react only after making physical contact. The diluent is a multicomponent halide melt

containing sodium ions. Figure 2(b) shows almost the same setup as Figure 2(a) but with one exception. The drop tubes containing K_2TaF_7 and sodium are electrically connected through an external circuit. This allows the reactions described by Equations 2 and 3 to proceed without physical contact between K_2TaF_7 and sodium. Electrons produced upon the formation of sodium ions according to Eq. 3 need not be donated directly to a contacting tantalum ion but instead can travel along the external conductor to the compartment containing K_2TaF_7 . In this case electrons produced by the ionization of sodium in the left chamber are transported through an external circuit to the fluorotantalate ions (TaF_7^{2-}) in the right chamber. There, they can reduce tantalum ions to metal. If such LREMR exists it should be manifest in the form of a current flowing in the external circuit. Furthermore, if LREMR is operative we should expect the production of tantalum powder to be confined to the right chamber where fluorotantalate is reduced due to the injection of electrons from the external circuit. LREMR is generally overlooked in the analysis of metallothermic reduction operations although it can be operative, if not dominant, in many instances.

(a) Metallothermic Reduction, or Short-Range-EMR



(b) Electronically Mediated Reacton, or Long-Range-EMR

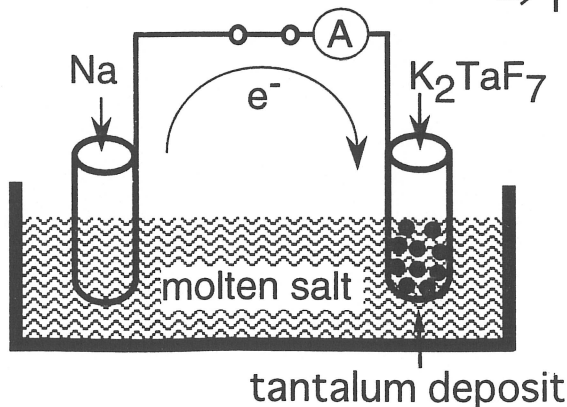
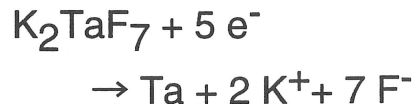


Figure 2. Design of experiment to prove the existence of long-range EMR.

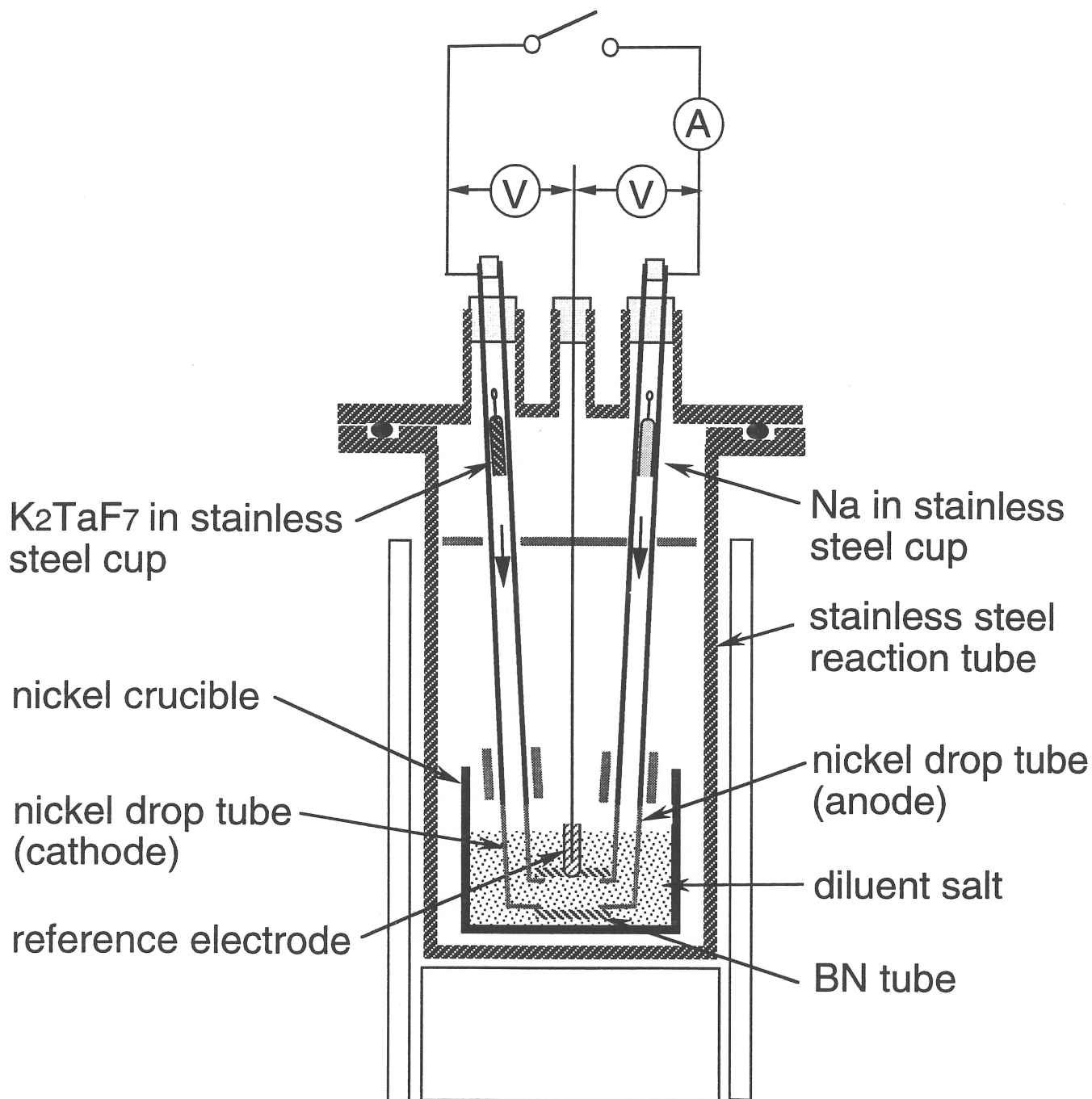


Figure 3. Experimental apparatus.

Figure 3 shows the experimental apparatus. The nickel drop tubes for the samples, boron nitride spacer, thermocouple sheath (not shown in the figure), two identical reference electrodes (only one shown in the figure), and the diluent salt were placed in the nickel crucible which measured 7.6 cm O.D. The reference electrode was a closed-one-end tube made of hot-pressed boron nitride. Inside was a nickel wire immersed in a melt consisting of the diluent salt to which NiF_2 was added to the level of 1 mol %. The bottom of the BN tube was milled down to a thickness of less than 1 mm to allow rapid establishment of electrical contact between the diluent salt and the melt in the reference electrode. About 440 g of diluent salt was charged into the nickel crucible. Prior to the experiment, K_2TaF_7 feed (mass 24.2 g) and sodium reductant (mass 12.8 g, which exceeds the stoichiometric

amount required by Eq. 1) were cast under argon atmosphere (grade 5.0, 1 ppm oxygen) into stainless steel cups. These cups were positioned at the top of the nickel drop tubes. The reaction tube was then assembled, evacuated to a pressure of 1 kPa, and heated to 400°C for 12 hours to remove moisture. The cell was back filled with argon, and the temperature was increased to 800°C. Once the diluent salt had melted, the reference electrodes were immersed into the diluent, and the external circuit was shorted. In some experiments, potassium was used as reductant. In such instances, the reaction temperature was reduced to 700°C to avoid boiling of the potassium metal.

The experiment began by dropping the cups containing the reductant and feed. Current was monitored in the external circuit by measuring voltage across a 1 m Ω standard resistor acting as a shunt. The data were taken by voltmeter (Keithley Model 181 Nanovoltmeter) and digital multimeter with eight-channel scanner (Keithley Model 199) and logged onto a PC via GPIB interface using software written in house. When the current in the external circuit dropped to below 0.5 A (typically this took about 2 hours) the experiment was terminated. The reference electrodes and the thermocouple were raised out of the diluent melt, and the power to the furnace was cut. The cell and its contents furnace-cooled to room temperature. Samples were taken of the solidified diluent and tantalum metal product. In total, about 10 g of tantalum was produced in a typical experiment. Metal powder was found throughout the channel formed by the nickel drop tubes and the boron nitride connector. Samples of this material were analyzed by x-ray diffraction and electron probe microanalysis.

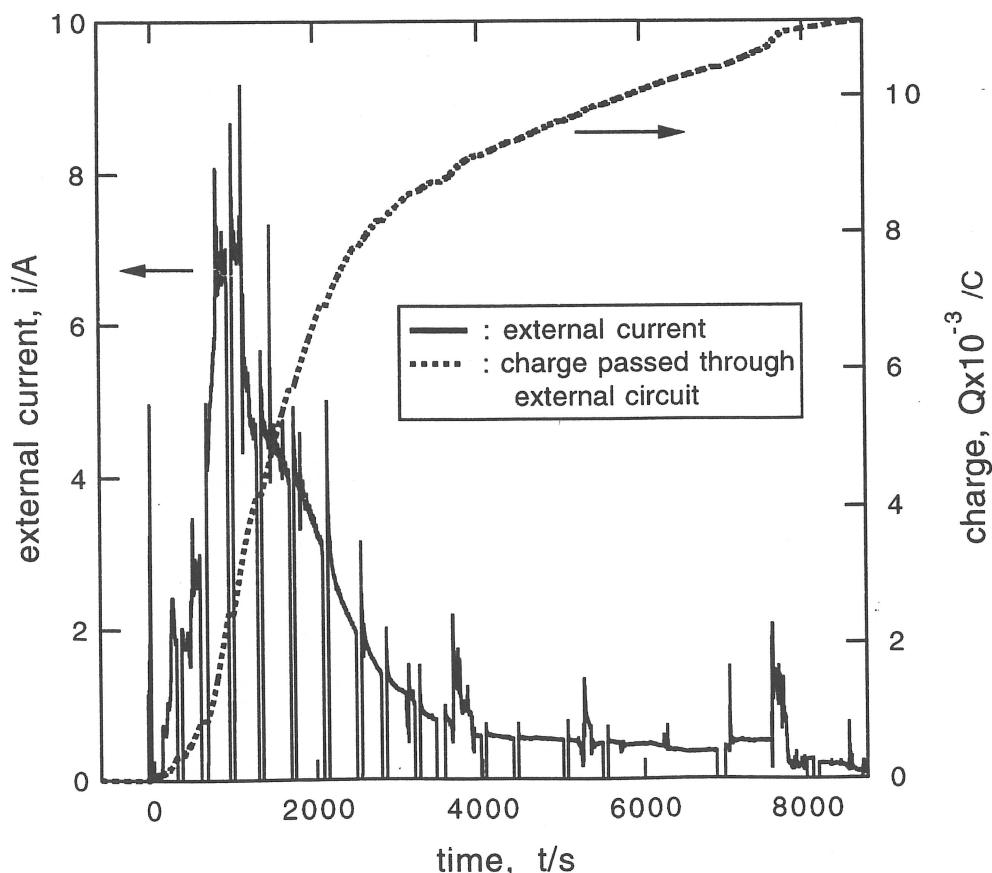


Figure 4. Measured current in the external circuit. Current spikes caused by occasional interruption of current to measure open-circuit potentials.

RESULTS

Figure 4 shows the current *versus* time trace for a representative experiment. Time zero is measured from the moment the feed and reductant were dropped into the diluent. Over the first 15 minutes the current rose steadily, reaching a maximum value of almost 8 A, and then decreasing over the next hour to below 1 A. The current spikes seen in the figure are experimental artifacts caused by occasional interruption of external current to allow measurement of the open-circuit potentials between the reference electrode and each drop tube. At the time of maximum current an open-circuit potential of 0.9 V was measured between the two drop tubes. The total electrical charge passed through the external circuit was calculated by evaluating the time integral of the current shown in Figure 4 and found to be 11100 C.

Clearly, the presence of current in the external circuit proves the existence of LREM — since feed and reductant are physically separated there is no way for the reaction to proceed by SREM. It takes 29800 C or 0.3085 moles of electrons to reduce completely 24.2 g of K_2TaF_7 (Ta^{5+}) to metallic tantalum (Ta^0). During the course of our experiment 11100 C passed through the external circuit. Therefore, at least 37% of the tantalum is produced by LREM, *i.e.*, without any direct physical contact between the K_2TaF_7 feed and the sodium reductant. In other words, it is the action of electrons donated by the sodium reductant to the electronically conductive medium in contact with both the sodium and the K_2TaF_7 feed that produces tantalum.

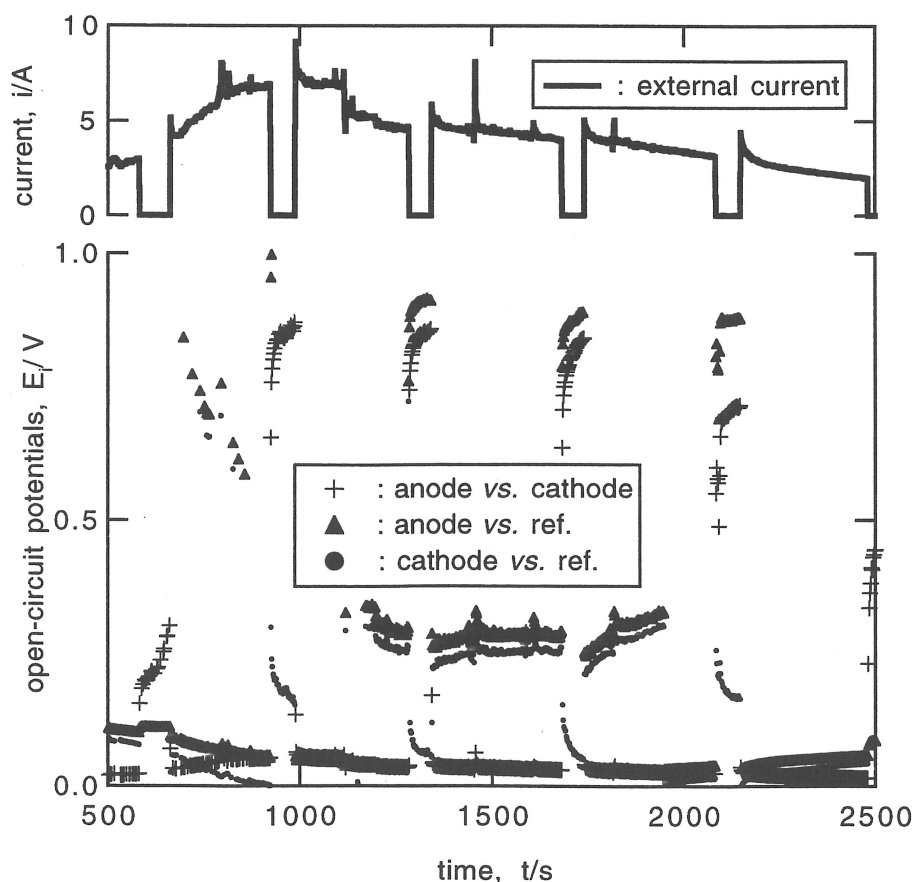


Figure 5. Measured open circuit potentials.

Figure 5 shows the variation of open circuit potentials during the course of an experiment. Periodically the current in the external circuit was interrupted, and voltages were measured (i) between the Ni/Ni²⁺ reference electrode and the K₂TaF₇ feed tube and (ii) between the Ni/Ni²⁺ reference electrode and the molten sodium. In the terminology of batteries, the K₂TaF₇ is acting as the cathode, while the sodium is acting as the anode. The driving force for the reaction between them was measured to be approximately 0.8 V. The Nernst potential calculated from the reported Gibbs free energy of formation of K₂TaF₇ is 1.4 V [12, 13]. Also, voltammetry in CsCl-KCl-NaCl-K₂TaF₇ melts shows a one-step reduction of Ta⁵⁺ to metal at a half-wave potential of 0.9 V *versus* Ag/AgCl. Given the expected electronic shorting caused by the high volatility of the metal reductant and possible degradation of the reference electrode in such a strongly reducing environment the measurement of somewhat lower voltages is judged to be reasonable under the circumstances.

Table I. Some representative conditions and results for metallothermic reduction of K₂TaF₇ by LREMR at 1073 K.

expt. no.	amount of reactant		temp. (°C)	reaction time (s)	observed current		charge through external circuit (C)	Ta fraction produced* by LREMR
	K ₂ TaF ₇ (g)	reductant (g)			max. (A)	average (A)		
1	39.1	12.6	800	14000	7	0.87	12200	25%
2	24.2	12.8	800	8600	8	1.29	11100	37%
3	16.4	12.2	700	3700	3	0.84	3100	15%
4	9.26	9.65 ⁺	700	4800	3	0.91	4400	38%

* percentage of K₂TaF₇ reduced by LREMR is calculated from the ratio of charge transported through the external circuit to total charge required to reduce all tantalum present in the feed

+ potassium was used as reductant.

Representative results of experiments demonstrating the existence of LREMR are summarized in Table I. In all cases, substantial currents were measured in the external circuit. By comparing the quantity of charge that passed through the external circuit to the total charge that would be required to fully react with the K₂TaF₇ reactant, the fraction of K₂TaF₇ that was reduced by LREMR was calculated. The results indicate that the extent of LREMR is not insignificant; in some experiments, almost 40% of the tantalum was produced by LREMR. The poor reproducibility may be attributed to leakage currents, which can be traced to the high vapor pressure of the metal reductant at the temperature of the experiment. This can also explain the surprisingly large fraction of tantalum produced by LREMR in experiment 4 when potassium, rather than sodium, was used as the reductant. Potassium was expected to be more soluble than sodium in the molten salt diluent with the result that the electronic conductivity is higher. This should increase the likelihood of SREMR, an expectation that was not supported by experimental evidence. Even with potassium as the reductant, the extent of LREMR was substantial.

In all cases, tantalum metal was found in the cathode tube and at the bottom of the crucible. Figure 6 shows how the morphology of the metal product is affected by the mechanism of the reduction reaction. Figure 6(a) shows fine, unagglomerated tantalum powder harvested

from the bottom of the crucible. This material is presumed to have formed by homogeneous nucleation in the diluent melt, which implies SREMR. Figure 6(b) shows the tantalum produced inside the fluorotantalate drop tube. This material is not loose powder but rather a compact deposit adhering to the metallic substrate. This is what one would expect for a metal produced by LREMR, which involves electron transport via a conducting intermediary substrate on which heterogeneous nucleation of tantalum metal occurs. These results indicate that two rather different types of metal product are formed depending upon the kinetic pathway.

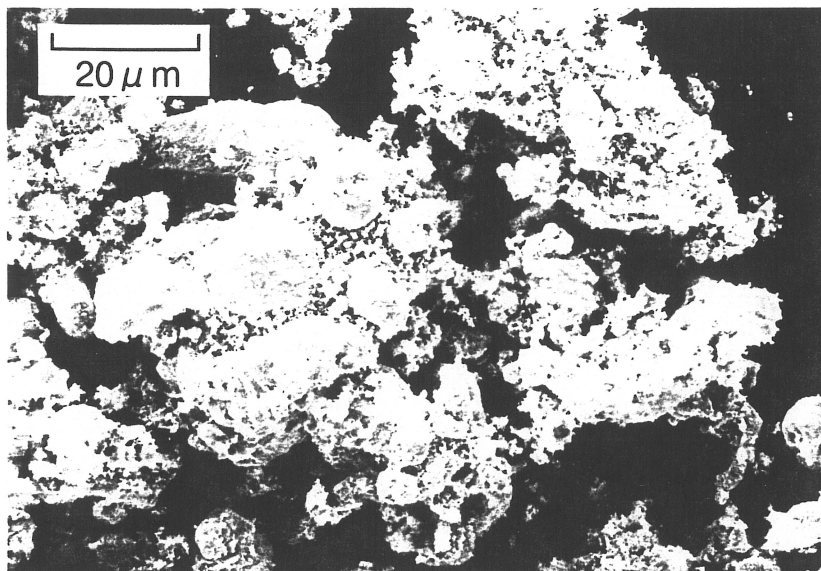


Figure 6. (a) Tantalum powder obtained from bottom of reactor vessel.

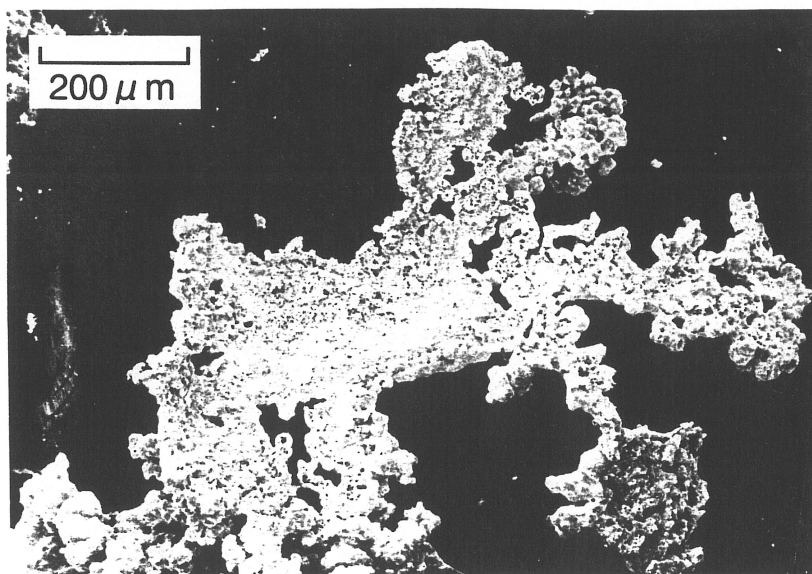


Figure 6. (b) Tantalum powder obtained in the cathode tube.

DISCUSSION

Industrial practice provides more evidence. In the Kroll process, titanium tetrachloride is reacted with magnesium to produce titanium metal in the form of sponge [14]. Because magnesium is almost insoluble in multicomponent melts containing magnesium chloride [15], there is effectively no electronic conduction in the melt [16]. Hence, the dominant kinetic pathway is LREM and the product metal is in the form of a dense, compact deposit known as sponge. In the Hunter process, titanium tetrachloride is reacted with sodium [17]. Here, titanium metal is produced mainly in powder form. At elevated temperatures sodium is quite soluble in sodium chloride [18]. Sodium dissolution is accompanied by electron solvation which enhances SREM and, hence, powder formation. Thus, it seems that the difference in the morphologies of Kroll and Hunter titanium can be explained by the difference in the electrical properties of the molten salt reaction media.

Table II: Recommended operating practices to tailor the characteristics of metal produced by metallothermic reduction

* powder *	* dense, compact metal *
☞ enhance SREM	☞ enhance LREM
1. mixing	1. no mixing
2. minimize the use of metal components	2. maximize surface area of electronically conductive medium
3. polarize metal anodically	3. polarize metal cathodically
4. charge with excess reductant, <i>i.e.</i> , in excess of feed	4. charge with excess feed, <i>i.e.</i> , in excess of reductant
5. render diluent electronically conductive	5. render diluent ionically conductive
6. mix feed and reductant in the charge	6. charge feed and reductant remotely

The results of this study can be generalized to other metallothermic reduction processes, to change either product morphology or process chemistry. Table II shows how to exercise morphological control over the product. For example, to make a dense, compact metal product requires that one take steps to ensure that LREM is the dominant kinetic pathway in order to enhance heterogeneous nucleation of new metal on selected substrates while repressing homogeneous nucleation of powders in the bulk of the diluent medium. In parallel, the level of electronic conduction should be kept at a minimum in the diluent salt. Practical measures include charging feed and reductant at different locations in the reactor and avoiding mixing. To minimize electronic conduction, feed should be charged in stoichiometric excess of reductant. Lastly, LREM can be further enhanced by cathodic polarization of the substrate on which metal product is forming.

Process chemistry can also be affected thanks to an understanding of the role of EMR in metallothermic reduction. Specifically, recognition of the effects of LREM opens up new possibilities in the choice of reductant. This is due to the fact that LREM occurs without direct contact between feed and reductant, thereby avoiding the undesirable effects of contamination of the metal product by impurities that may be present in the reductant. For example, one can imagine a process in which titanium tetrachloride is reacted with

magnesium scrap to produce titanium metal. If the reaction is controlled so as to proceed strictly by LREM (this can be managed by reactor design), the reductant can be physically separated from the feed and thus there is no danger of contaminating the product metal with impurities and alloying elements present in the magnesium scrap. Using magnesium scrap instead of high-purity magnesium or sodium as the reductant offers significant cost advantages and is at the same time environmentally friendlier than the present technology. In the absence of an understanding of LREM, use of magnesium scrap in this application would be unthinkable. In other words, the old adage of process metallurgy has been overturned. Previously it was thought that to make high-purity product required high-purity feed *and* high-purity reductant. Understanding LREM points the way to processes in which it may be possible to make high-purity product from high-purity feed and *low-purity* reductant. Verification awaits further research.

SYNTHESIS OF INTERMETALLIC COMPOUNDS BY REDUCTION OF MULTICOMPONENT SOLUTIONS OF LIQUID AMMONIA

Ammonia dissolves alkali metals. For example, sodium will dissolve in liquid ammonia to give Na^+ and a solvated electron. The result is a medium that is very potent for chemical reactions involving metathesis reduction where it is known that the slow step is not mass transport, *i.e.*, transport of reagents, but rather, electron transport, *vide supra* [19]. We have investigated whether it is possible to make tantalum powder by reacting a solution of TaCl_5 dissolved in liquid ammonia with a solution of Na dissolved in liquid ammonia. While in the absolute, sodium should reduce TaCl_5 , in the presence of liquid ammonia there is the possibility that instead of tantalum metal, the product of reaction is some tantalum amine compound. Our study has shown that indeed tantalum metal forms. The advantage of this process is that because the temperature of reaction is -40°C , the particle size of the tantalum powder is much finer than that produced by conventional technology which operates at much higher temperatures (near 850°C). We have made powder that averages 20 nm in diameter, far less than the micron-sized material produced by the industrial process.

Beyond this, we have tried co-precipitation/co-reduction of metals by first dissolving multiple compounds of the metals in liquid ammonia and then reducing the solution to promote the precipitation of a heteronuclear compound product. For example, both NbCl_5 and AlCl_3 were dissolved in liquid ammonia. To this solution of the two salts a solution of Na dissolved in liquid ammonia was added. The sodium reacted with the binary salt solution to produce a dispersion of fine powder, which appears to be the intermetallic compound of niobium and aluminum, Nb_3Al . Why do we believe this to be so? It is known that AlCl_3 is not reduced by Na metal dissolved in ammonia. However, in our experiment with the solution containing *both* NbCl_5 and AlCl_3 , the mass balance on the NaCl product indicates that there is more chlorine present in NaCl than could be obtained from reducing all the NbCl_5 . This means that some AlCl_3 must have been reduced. One explanation is that by forming the compound the chemical potential of Al is reduced to the point where it becomes viable to produce it by reduction of AlCl_3 . Put another way, it is only through compound formation that Al reduction is possible.

Can we imagine other compounds that can be produced in the same manner? Yes, TiB_2 and GaN are two examples.

CONCLUSIONS

The production of tantalum powder by the reaction of K_2TaF_7 with sodium has been studied, and two dominant kinetic pathways, both involving electron transfer, have been found. Electron transport between reactants can be rate limiting; hence, the reaction is considered to be electronically mediated. The location of the tantalum deposit and its morphology seem to depend on the reaction pathway. Recognition that metathallotermic reduction is electronically mediated is helpful for the design of new processes and optimization of existing processes. It would be interesting to test on a wider basis the concepts set forth in the present article; specifically, analysis of other metathallotermic reduction processes within the framework of electronic mediation could prove insightful.

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