The Electrochemical Processing of Refractory Metals

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Electrochemical processing is used extensively in the primary extraction of metals (electrowinning), the purification and recycling of metals (electrorefining), and the formation of metal coatings (electroplating). With respect to the refractory metals, electrochemical processing is conducted almost exclusively in nonaqueous media, predominantly in molten salts. Electrolysis in fused salts as well as other nonaqueous media has enormous potential for materials processing. First, because of the special attributes of nonaqueous electrolytes, electrochemical processing in these media has an important role to play in the generation of advanced materials—materials with specialized chemistries or tailored microstructures (electrosynthesis). Second, as environmental quality standards rise beyond the capabilities of classical metals extraction technologies to comply, electrochemical processing may prove to be the only acceptable route from ore to metal.

INTRODUCTION

The refractory metals comprise the elements Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. They are also known as the transition elements and are found in the periodic table in Groups 4, 5 and 6. Although metallurgists find it convenient to refer to the refractory metals as a class, their distinctive electron configurations give each element a character of its own. The exception is the zirconium-hafnium pair. Because of the lanthanide contraction, the heavier two elements of each group are nearly identical in size. However, unlike niobium-tantalum and molybdenum-tungsten, zirconium and hafnium have identical outer shell electron arrangements—[Kr]$4d^25s^2$ for zirconium and [Xe]$4f^{145}5d^26s^2$ for hafnium—and thus exhibit nearly identical chemical behavior. As a result, it is rather difficult, for example, to produce hafnium-free zirconium as required in nuclear-reactor applications. Appreciation of the electronic structure is important in the search for new processes for extracting, purifying and recycling these metals.

The phrase "refractory metals" is misleading in some respects, for these elements are rather reactive and form very stable (high melting point) compounds that exhibit an interesting array of properties. For example, the borides and nitrides are excellent electronic conductors; the electrical conductivities of both TiB_2 and TiN exceed that of titanium metal itself. For their heat and erosion resistance, the carbides find use as constituents of cutting tools. The silicides are used as heating elements in electrical resistance furnaces for service at elevated temperatures under oxidizing conditions. The compounds comprising the borides, carbides, nitrides and silicides of the refractory metals are known in some circles by the name refractory hard metals. This reflects the fact that although these substances are, strictly speaking, compounds and not metals, in many of their properties they exhibit metallic behavior.

Many of the refractory metals are present in the Earth's crust in relatively large proportions.[1] For example, Ti, Zr, Cr and V rank above Zn, Ni and Cu in relative terrestrial abundance. Tungsten is more abundant than tin. Niobium is more abundant than lead. In spite of this, many of the refractory metals are considered strategically important by the United States, which, for five of the nine refractory metals, imports more than 50 percent of its requirements.[2]

With the exception of molybdenum, the refractory metals are extracted primarily from oxygen-bearing minerals. For example, titanium is extracted from ilmenite ($FeTiO_3$) and rutile (TiO_2), zirconium comes from zircon ($ZrSiO_4$), vanadium is taken from a number of vanadates, niobium and tantalum are extracted from mixed niobate-tantalate ores, chromium is extracted from chromite ($FeCr_2O_4$), and tungsten comes from tungstates. Molybdenum, in contrast, is primarily extracted from the sulfur-bearing mineral molybdenite (MoS_2).

The primary extraction of refractory metals can be accomplished in two ways: thermochemical and electrochemical. One form of thermochemical extraction, practiced especially with metals in Groups 4 and 5, involves the metallothermic reduction of a compound containing the refractory metal. The compounds are oxides, fluorides or chlorides; the reductant is chosen from among aluminum, magnesium, sodium and calcium, although other reactive metals have been used. For example, titanium metal is produced by the Kroll process, which is based upon the reaction of titanium tetrachloride with magnesium:

$$TiCl_4 + 2Mg = 2MgCl_2 + Ti \qquad (1)$$
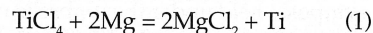
For the production of a ferroalloy such as ferrochrome, reduction by carbon in an electric furnace is employed. In another form of thermochemical extraction, practiced mainly with metals in Group 6, the refractory-metal sulfide is roasted to convert it to oxide, which is then reduced to metal by hydrogen.

Electrochemical extraction involves the electrolytic reduction of a refractory-metal compound dissolved in an ionic medium. Why, then, fused-salt electrolysis? Unfortunately, aqueous solutions are unsuitable as electrolytes for the electroreduction of the refractory metals, with the exception of chromium. At decomposition potentials negative enough to deposit these elements, hydrogen evolution occurs. To a first approximation, aqueous electrochemistry is restricted to the energy window bounded by the hydrogen and oxygen evolution reactions. Kinetic factors extend these limitations somewhat, but not far enough to allow electrolysis of the highly reactive refractory metals and their compounds. Hence, there is a need to exploit nonaqueous electrolytes.

There are three categories of nonaqueous electrolytes, characterized primarily by their temperature regime of stability: at ambient temperature, organic electrolytes; at elevated temperatures, molten salts; and at subambient and cryogenic temperatures, liquefied gases. This article discusses molten salts and liquefied gases. In metallurgical applications, organic electrolytes play a very small role. This is, in part, a consequence of their poor ionicity, which results in low electrical conductivity and the inability to dissolve reactants. Additionally, organic electrolytes may be carcinogenic, have a low flash point, or react violently with water.

By way of introduction to the field of molten salts, the reader is directed to the collections by Blander,[3] Sundheim,[4] Mamantov,[5] and Mamantov and Marassi,[6] as well as the monographs by Lumsden[7] and Bloom.[8] A brief overview can be found

in the two-volume set by Richardson.[9] The electrochemistry of molten salts is treated in the monograph by Delimarskii and Markov.[10] Basic property data have been compiled by Janz in a handbook[11] with supplements published in the *Journal of Physical and Chemical Reference Data* (see References 12 and 13, for example). The properties of the most common solvent systems have been collected by Plambeck.[14] The industrial applications of molten salts are treated in books edited by Lovering[15] and Kuhn.[16]

Current research and reviews are reported in several series, including *Advances in Molten Salt Chemistry*[17] and *Molten Salt Techniques*,[18] as well as in proceedings volumes from international symposia held under the umbrella of the Electrochemical Society.[19] As for archival publications, the journals where molten salt research is apt to be reported include the *Journal of the Electrochemical Society*, *Electrochimica Acta* and the *Journal of Applied Electrochemistry*. There is a substantial amount of activity in the Soviet Union, with the result that much of the molten salt literature is not published in English (e.g., *Rasplavy [Melts]*, published in Sverdlovsk, and *Ukrainskii Khimicheskii Zhurnal [Ukrainian Journal of Chemistry]*, published in Kiev). The international molten salt community meets regularly on several biennial timetables: at symposia held during meetings of the Electrochemical Society (the last one was held May 1990 in Montreal, Canada); at the Gordon Conferences under "Liquid Metals and Molten Salts" (the next one will be held August 1991 in New Hampshire); at conferences on molten salts sponsored by EUCHEM, the European division of IUPAC (the last one was during September 1990 in Patras, Greece); and, finally, every four years at the International Symposium on Molten Salt Chemistry and Technology (the latest one is scheduled for this month in Paris).

ELECTROWINNING AND ELECTROREFINING

This brief review reports advances cited in the literature since 1978. For an accounting up to that time, the reader is directed to earlier reviews, such as that by Inman and White.[22]

With the exception of titanium, the primary extraction of refractory metals by fused-salt electrolysis has received limited attention. Reports of research have been published on fused-salt electrolysis for processing titanium,[23–27] zirconium,[28,29] hafnium,[30] vanadium[31] and tantalum;[32] one patent treats the technology in general.[33] The preparation of high-purity metal and recovery of scrap, both by fused-salt electrorefining, have been studied for titanium,[34–36] zirconium,[37,38] niobium,[39,40] and Group 4 and 5 metals.[41]

Along with the extraction and refining processes themselves, various aspects of molten salt chemistry and electrochemistry have been investigated. Topics include electrolyte optimization,[42,43] anodic reaction,[44] chronopotentiometry,[45,46] disproportionation,[47] voltammetry[46,48–50] exchange-current density measurements,[51] phase-diagram determinations,[52,53] and vapor-pressure measurements.[53,54] Laboratory-scale electrolysis cells have been operated to investigate how process parameters affect current efficiency.[55] Finally, attempts have been made to construct mathematical models of the electrolysis process.[56]

ELECTROPLATING

Fused-salt electrolysis can also generate coatings containing refractory metals. The range of compositions includes elements, alloys and compounds. Indeed, the electroplating of refractory metals has received somewhat more attention than electrolytic extraction. At least on the basis of reports in the open literature, the most thoroughly studied metals from the perspective of electroplating are molybdenum[57–60] and titanium.[61,62] However, other metals, including niobium,[63,64] tantalum,[63,65,66] chromium[67–70] and tungsten,[71] continue to receive attention. Electrodeposited coatings can be pure metals, metal alloys or compounds. Alloys described in recent reports on electrodeposition include Mo-Nb,[72] Ni-Ta[73] and Ni-Nb.[73]

As for the electrodeposition of compounds containing refractory metals, the earliest work was concentrated on the production of carbides, largely for the purposes of generating abrasion-resistant


CHARACTERISTICS OF FUSED-SALT ELECTROLYSIS

Electrolysis is an electrochemical process (i.e., a process in which chemical reaction is accompanied by electron transfer). Electrolysis is performed in a reactor called an electrochemical cell, which is a device that enables electrical energy to do chemical work. In the context of this article, that chemical work is the extraction of elemental metal from one of its compounds. The compound, in turn, must first be dissolved in a fused-salt solution from which metal is recovered by the passage of electrical current. Figure A shows a prototypical molten-salt electrolysis cell. Its principal components are the electrolyte, the electrodes and the container (sidewalls and floor). The electrolytes are multicomponent melts of either chlorides or fluorides.

Chlorides offer the advantages of a lower operating temperature and of a greater choice of electrode and container materials. As for disadvantages, chlorides react with moisture: some are hygroscopic, even deliquescent, while others decompose by hydrolysis. Hydrolysis prevents dehydration—simple heating will not result in the removal of the water of hydration from niobium pentachloride:

$$NbCl_5 \cdot H_2O = NbCl_5 + H_2O \qquad (2)$$
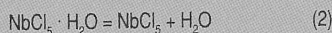
Instead, hydrolysis occurs to convert the pentachloride to oxychloride with attendant emission of hydrogen chloride gas:

$$NbCl_5 \cdot H_2O = NbOCl_3 + 2HCl \qquad (3)$$
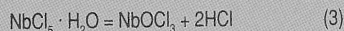
Niobium oxychloride ($NbOCl_3$) is much stabler than $NbCl_5$ and is, thus, much more difficult to electrolyze. Further, $NbOCl_3$ contains oxygen, which at the carbon anode reacts in preference to chlorine and forms carbon monoxide and carbon dioxide. The result is an increase in the anode consumption rate. To assure metal purity, it is imperative that the electrolyte be free of the impurities formed by reaction with moisture. This adds to the number of unit operations in the preparation of cell feed from source materials and puts strict requirements on the operating conditions of the electrolysis cell.

Fluorides, on the other hand, have the advantage of being less reactive with moisture. Additionally, fluorides can dissolve oxides directly. This avoids fluorination, which requires reaction with ammonium bifluoride, for example. In principle, the use of an oxide-based cell feed simplifies the process flowsheet and reduces capital and operating costs. Unfortunately, the higher melting points and greater corrosivity of the fluorides severely limit the choice of materials of construction in the physical plant. Another disadvantage is the relatively low solubility of refractory-metal oxides in molten fluorides. Because the limiting current density scales directly with concentration, the low solubility of oxide feed in fluoride melts limits cell productivity by setting a rather low ceiling on the maximum practical operating current density.

During electrolysis, electric current is passed from the anode through the electrolyte to the cathode. The electrolyte must be strictly an ionic conductor, while the electrodes must be electronic conductors. The anode can be either consumable or nonconsumable. Consumable anodes are found in various electrolytic processes. In electrorefining, the anode consists of an impure form of the metal to be purified. In electroplating, the consumable anode may act as the feedstock for the deposited metal. In electrowinning, the consumable anode consists of a material that reacts with the products of the anodic reaction (e.g., a carbon anode in the presence of evolving anodic oxygen).

Used primarily in electrowinning, nonconsumable anodes consist of materials inert to chemical and electrochemical attack. In chloride electrolytes, carbon commonly serves as a nonconsumable anode. There is no fully satisfactory nonconsumable anode for use with fluoride-based electrolytes. For the Hall cell—used in the electrolytic extraction of aluminum—the author has defined a new approach for discovering nonconsumable anodes for use in fused-salt electrolysis operations and has described the relevant set of selection criteria.[20]

As for cathode materials, carbon, refractory metals (such as tungsten, molybdenum and tantalum) and low-carbon steel have all been employed. In practice, the cathode functions only as the current lead. During electrolysis, the cathode material is separated from the electrolyte by the product refractory metal, which is produced in solid form unless a low-melting metal is employed as a liquid cathode.

There are advantages and disadvantages to producing either solid metals or liquid alloys. When the cell product is solid metal, it is not necessary to purify it of large amounts of host cathode metal. The disadvantage is that solid metal deposited from molten salts is invariably dendritic. This results in salt entrainment with the need for some form of subsequent treatment for salt removal. The production of liquid metal solves the morphological problem and facilitates the easy removal of the product from the cell by siphoning; however, this approach has its faults—the principal one being the need to refine the refractory metal out of the product cathode metal alloy.

The electrolyte is contained in a steel shell lined with carbon block. With chlorides, a lining of ceramic or low-carbon steel is acceptable. It is also possible to operate with a sidewall of frozen electrolyte. Current densities are about 1 A/cm² for electrowinning molten metal; for reasons related to assuring morphological stability, current densities in electroplating cells are about an order of

coatings.[71,74] Coatings of titanium diboride have been deposited both to impart corrosion resistance against attack by liquid metal[75,76] and to offer abrasion resistance.[77–79] More recently, investigators have begun studying the associated electrode processes.[80] Generation of tungsten carbide coatings has been driven by the desire to form material for use in abrasion-resistant coatings.[71,81–83] Studies of electrochemical fundamentals have begun.[84,85] Other refractory metal compounds whose electrosynthesis has been reported include zirconium diboride,[86] chromium boride,[87] molybdenum disilicide,[88] tantalum carbide[89] and molybdenum carbide.[90]

More recently, attention has turned to a broader array of materials syntheses, including metal-matrix composites[91] and refractory-metal oxides containing con-trolled subvalent forms of the refractory-metal ion.[92] In the case of the latter, electrosynthesis from fused salts has facilitated the generation of compounds otherwise produced thermochemically at high temperatures and high pressures.

An alternative to the electrosynthesis of refractory-metal oxide compounds is anodization. The distinction between the two processes is that anodization is a process for the faradaic oxidation of elemental metal present as the anode substrate. In contrast, electrosynthesis is a process for the faradaic discharge of both metal and oxygen (both of which are present in the electrolyte) to form a compound on an electrode substrate. While refractory metals can be anodized in aqueous media, fused-salt anodization offers certain advantages in product quality, both in terms of chemical composition and microstructure.[93]

Cryogenic Electrolytes

Cryogenic electrolytes do not appear in contemporary metallurgical technology. Electroplating of elemental refractory metal from subambient and cryogenic liquids has been reported but not at the commercial scale.[94] At the time of this writing, the viability of electrosynthesis of compounds in cryogenic media is under investigation at the Massachusetts Institute of Technology.[95] Later in this article, reference will be made to future prospects for electrochemical processing in these media.

FUTURE DIRECTIONS

When viewed in the context of materials processing, fused-salt electrolysis has many fine attributes. However, unresolved technical issues continue to impede its further commercialization. These include low cathode current efficiency, the anode effect (restricted to fluoride-based electrolytes processing oxide feed), the purity of the product, the corrosion of cell components and the heat balance of the cell. Losses of power efficiency can be traced to the fact that the refractory metals exhibit multiple valency in these melts. This can lead to redox looping or parasitic reaction of subvalent ions with metal product.

Further, as mentioned above, most cells produce solid metal. Solid electrodeposits obtained in molten salts are typically dendritic or powdery, but rarely smooth, especially when the metal is of high purity. To deal with multiple valency, one can optimize bath chemistry,[42,43] use a diaphragm to separate specified ions from one another while allowing selected mass transfer between regions of the cell (an approach very popular with designers of titanium electrowinning cells),[96–98] or invent divided cells featuring staged reactions.[99] The morphological problem has been attacked in some cases by employing molten metal cathodes (see References 33 and 100, for example). The use of leveling agents, while potentially beneficial, has been examined for electroplating[57] but, evidently, not for electrowinning, where the goal is to produce metal of the highest purity.

Besides the strictly technical issues, there are other concerns. For example, in designing new electrolytic processes, one must look carefully at capital costs as well as operating costs. If fused-salt electrolysis is to compete effectively with non-electrochemical extraction processes, steps must be taken to design flow sheets with a minimum number of unit operations. More attention must be paid to environmental, health and safety issues. For example, in the production of titanium, whether by the Kroll process, the Hunter process or molten chloride elec-
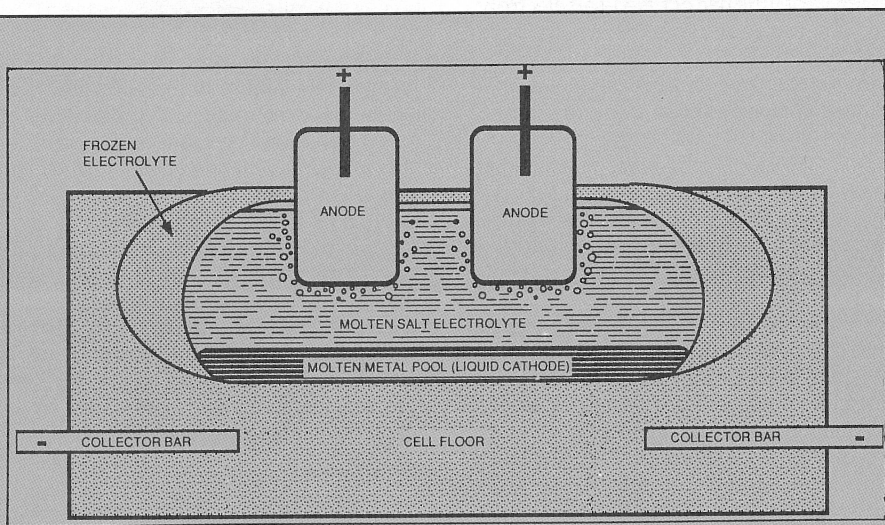

Figure A. A prototypical electrolysis cell.

magnitude lower and range from 10–100 mA/cm². Cell operating temperatures span 400–1,000°C. Cell voltages depend upon the particular melt chemistry and cell design, which determines the contribution of the ohmic resistance of the bath. During electrolysis, the voltage required to drive the process is substantially higher than the reversible potential as calculated by the Nernst equation, which for metal halide (MX_n) in a multicomponent molten salt solution and in equilibrium with pure metal (M) and pure gas (X_2) at atmospheric pressure can be expressed as the following:

$$E_{MX_n} = -\Delta_f G^\circ_{MX_n} / (nF) - (RT / nF) \ln a_{MX_n} \quad (4)$$

where $\Delta_f G^\circ_{MX_n}$ is the standard Gibbs free energy of formation of MX_n, F is the Faraday constant (96,487 C/mol), R is the gas constant [8.314 J/(mol·K)], T is the temperature in Kelvins and a_{MX_n} is the activity of MX_n in the electrolyte solution. E_{MX_n} is a function of electrolyte composition and temperature. The difference between the equilibrium potential and the applied voltage is due to kinetic factors which increase the energy consumption of the cell. The cell voltage for the electrolytic decomposition of MX_n is given by Equation 5:[21]

$$V_{cell} = E_{MX_n} + (\eta_a + \eta_c)_{cathode} + (\eta_a + \eta_c)_{anode} + \eta_{electrodes} + \eta_{ohmic} \quad (5)$$

where E_{MX_n} is the reversible potential or equilibrium decomposition potential given by the Nernst equation; η_a is the activation overpotential at the electrode and is a function of electrolyte composition, current density and temperature; η_c is the concentration overpotential at the electrode and is a function of electrolyte composition, current density and temperature; $\eta_{electrodes}$ includes the voltage drops associated with the electrodes themselves, with the bus bars and with the electrical contacts between them; and η_{ohmic}, the ohmic overpotential or IR drop, is due to the electrical resistance of the electrolyte itself and is proportional to current density and interelectrode distance and inversely proportional to the electrical conductivity of the electrolyte and to the electrode area. Existing industrial molten salt electrolysis cells operate at voltages three to five times the value of the Nernst potential.

Cell productivity is expressed in terms of several figures of merit. Current efficiency can be loosely defined as the ratio of the number of equivalents of metal product to the number of moles of electrical charge delivered to the cell by the power supply. As such, current efficiency is effectively a measure of compliance with Faraday's laws of electrolysis. In electrowinning cells, cathodic current efficiencies of 60 percent to 80 percent are not uncommon. These figures are well below those reported for the electrolytic production of aluminum, which typically attains current efficiencies exceeding 90 percent.

Voltage efficiency is the ratio of the equilibrium decomposition potential to the applied cell voltage. Quite simply, voltage efficiency expresses the deviation from the Nernst equation and is a measure of inefficiency due to kinetic factors cited above. In the electrolysis of fluorides, voltage efficiencies are typically below 50 percent, while in the electrolysis of chlorides values below 25 percent have been reported.

trolysis, TiO_2 must be converted to $TiCl_4$. This is accomplished by carbochlorination:

$$TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2 \quad (6)$$
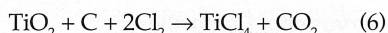
This is a carbon-intensive process that requires metallurgical coke. In addition, metal produced in a Kroll reactor is in the form of sponge, which must be acid leached to remove entrained salt and unreacted magnesium. Coking and acid leaching are becoming less attractive from an environmental standpoint. Clearly, the ecological soundness of new processes must be considered from the time of their invention. Molten salt electrolysis is uniquely positioned to tackle these problems that, if left unsolved, threaten to cripple the metals industry.

At the Massachusetts Institute of Technology, this author has begun a major initiative to develop a suite of environmentally sound metal-extraction technologies based upon direct electrolysis at very high temperatures. The concept, called pyroelectrolysis, uses molten oxides as electrolytes. Operating temperatures are high enough so that the product metal is liquid, not solid, as is the case with all other electrolytic technologies producing refractory metals. In deference to industrial ecology, the process is designed to be carbon-free—carbon is not used as a reagent in the preparation of cell feed or as a constituent of the electrodes in the electrolytic cell. The gas by-product is pure oxygen. With fewer unit operations, the process offers the prospect of lower capital cost than conventional extraction technologies now in place. Pyroelectrolysis appears to be broadly applicable to the extraction of a wide range of metals, including refractory metals, transition metals (Fe, Co, Ni and Mn), lanthanides (rare-earth metals) and actinides (uranium, in particular). As for specific metals, work is currently under way to determine the feasibility of direct electrolytic extraction of titanium from TiO_2.

Titanium was chosen for two reasons. First, it is the most abundant of the refractory metals and has the greatest near-term market potential. Second, all currently employed technologies for the extraction of titanium are directly or indirectly electrolytic technologies. In order to be recycled, the metal reductant in the Kroll and Hunter processes is recovered by molten-salt electrolysis. Thus, the capital and operating costs of electric power are already built into all titanium extraction technologies. Against this backdrop, the economics of the pyroelectrolysis of titanium look very attractive. Direct electrolytic steelmaking is also under study, with a special focus being placed on ferroalloys such as ferrochrome and ferromanganese.

From the perspective of a technology capable of generating advanced materials, fused-salt electrolysis looks attractive.[101] Advanced materials are characterized not only by their specialized chemistries (e.g., purity, doping level, etc.), but also by their tailored microstructures, which fused-salt electrolysis has the potential to generate. These include thin films, epitaxial layers, powders and various nonequilibrium structures. Powders of a number of refractory metals and their compounds have been produced by fused-salt electrolysis; among those produced are titanium,[102–104] niobium,[105] tantalum,[105] chromium,[103] tungsten[103,106] and tungsten carbide.[83] A French patent describes a process for producing a number of refractory metal powders.[107] As for nonequilibrium structures, fused-salt electrolysis has the capacity to produce metastable phases, compositionally graded microstructures and compositionally modulated microstructures. To date, there has been very little use of fused-salt electrolysis to generate nonequilibrium structures of refractory metals. There are isolated reports in the literature of metastable-phase formation[108] and deposition of single crystals with preferred orientation.[109] These results were restricted to refractory metals and not their compounds. Among the layered structures reported in the literature is molybdenum carbide on diamond.[110] Overall, this field is severely under exploited.

Earlier in this article, liquefied gases were named as a class of inorganic electrolytes. What is their potential role in the electrosynthesis of advanced materials? What is to be gained by processing in such media? First of all, these electrolytes are anhydrous and chemically stable. Thus, in principle, one should be able to electrodeposit elements that cannot be plated from aqueous solutions. Second, the processing temperatures are very low, with the result that thermal damage to the substrate is minimized. Third, at these low processing temperatures, the kinetics of deposition are expected to be controlled by charge transfer rather than by mass transfer. This tends to favor surface smoothing and the production of coatings of uniform thickness; alternatively, the process can be said to have good throwing power.

There are other microstructural consequences. Low-temperature processing enhances nucleation and restrains growth. Deposits are expected to be microcrystalline or, perhaps, even amorphous. If sharp interfaces are sought, electrodeposition at cryogenic temperatures is unique in that it is a process operative at low temperatures and driven by low energy. Diffusion distances are extremely short; diffusion times are extremely long. These are precisely the process characteristics necessary for materials processing at nanoscalar dimensions. Fourth, the preparation of the electrolyte involves the condensation of a gas with the result that the solutions have the potential to be uncommonly free of contaminants. This puts cryogenic electrolytes at an advantage over high-temperature electrolytes, which tend to dissolve, albeit sparingly, even the most refractory crucibles. When high purity is a concern, cryogenic electrolytes are excellent processing media.

As a consequence of the fact that the database for these media is almost nonexistent, cryoelectrodeposition has been conducted largely on an empirical basis. Much vital information is unreported, including compound solubilities and decomposition potentials, which are essential in describing the chemistry and electrochemistry of the process. Even the state of the metallic ion in solution is unknown. There is much to be done in researching the physical chemistry of these liquids before commercial viability can be properly assessed.

CONCLUSION

While molten salt electrolysis has proven its viability in metallurgical processing, the technological applications of electrochemical processing in nonaqueous media have not been exhausted. The pyroelectrolytic extraction of metal in molten-oxide electrolytes and the electrosynthesis of refractory metal compounds in cryogenic electrolytes both represent enormous commercial potential. Finally, as environmental quality standards rise beyond the capabilities of classical metals extraction technologies to comply, direct electrolysis may prove to be the only acceptable route from ore to metal.

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