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THE SYNTHESIS OF REFRACTORY-METAL COMPOUNDS BY ELECTROCHEMICAL PROCESSING IN NONAQUEOUS MEDIA

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Abstract

Electrochemical processing in nonaqueous media has an important role to play in synthesizing refractory-metal compounds in large part due to the following processing conditions: a wide choice of temperature from high-temperature fused salts to low-temperature cryogenic liquids; a wide potential window (different emf series) which allows access to reactive elements. In addition to specialized chemistries, electrolysis has the potential to generate materials with tailored microstructures: thin films, epitaxial layers, powders of controlled particle size, and nonequilibrium structures such as compositionally graded and compositionally modulated microstructures. The characteristics of fused salt electrolysis are presented. The prospects of commercialization are assessed in the light of unresolved technical issues.

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Introduction

The refractory metals comprise the elements titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten. They are also known as the transition elements and are found in the Periodic Table in Groups 4, 5, and 6¹. In some respects the term, refractory metals, is misleading, for these elements are rather reactive and form very stable (high melting point) compounds exhibiting an interesting array of properties. For example, the borides and nitrides are excellent electronic conductors: the electrical conductivity of both TiB₂ and TiN exceeds 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 suite of compounds comprising the borides, carbides, nitrides and silicides of the refractory metals is 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.

Chemical synthesis of refractory metal compounds is not trivial. Refractory metals exhibit multiple valency and in many cases their compounds are nonstoichiometric. Thus, controlling the composition of a compound formed by reaction of a refractory metal with a gas containing the nonmetallic constituent is very difficult. Electrochemical synthesis offers, in principle, the means to address this and other problems with conventional methods.

Why, then, nonaqueous media for electrosynthesis of refractory metal compounds? Unfortunately, aqueous solutions are unsuitable as electrolytes for the electroreduction of the refractory metals, with the exception of chromium. At decomposition potentials electronegative 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, the need to exploit nonaqueous electrolytes, of which there are three categories, characterized primarily by their temperature regime of stability: at ambient temperature, organic electrolytes; at elevated temperatures, molten salts; at subambient and cryogenic temperatures, liquefied gases. This article is confined to a discussion of the latter two. In metallurgical applications organic electrolytes play a very small role. This is in part due to their poor ionicity which results in low electrical conductivity and inability to dissolve reactants. As well, organic electrolytes can have some or all of the following characteristics: low flash point, carcinogenic, react violently with water.

The purpose of this article is to describe the theory and practice of fused salt electrolysis as it applies to the electrochemical synthesis of refractory metal compounds. In addition, the potential of cryogenic electrolytes to synthesize advanced materials will be assessed.

¹ In this article the periodic notation follows recent recommendations by IUPAC and ACS nomenclature committees. To eliminate ambiguity A and B designations are avoided. Groups IA and IIA are denoted 1 and 2, respectively, the d-transition elements groups 3 through 12, and the p-block elements groups 13 through 18. In the last digit the former Roman numeral designation is preserved, e.g., IV → 4 and 14. So Ti, Zr, and Hf become Group 4, while C, Si, Ge, Sn, and Pb become Group 14.

This author has published previous work on the following topics:

Electrolysis is a process by which a substance is decomposed by electron transfer. It is a device that is used to separate a substance into its chemical components. It is the chemical reaction that occurs when a substance is dissolved in an electrolyte and a current is passed through it. The products of the reaction are the metal and the nonmetallic constituent. The products are metal halides, chlorides, and tungstates.

During electrolysis, the metal is deposited at the cathode. The metal must be electrochemically active. In chloride electrolysis, the metal is deposited as a chloride. In reference to the metal, the metal is deposited along with the metal.

As for cathode, the metal is deposited as well as low current lead a product re

The electrolyte is a ceramic or low conductivity electrolyte. The electrolyte determines the neighborhood

Cell productivity is loosely defined as the amount of electrical energy effectively used in a defined area. It is simply, voltage efficiency due to the use of bus bars, and each electrode

Characteristics of Fused Salt Electrolysis

This author has recently reviewed the fused salt electrolysis of rare earth metals (1). The following account of the characteristics of fused salt electrolysis is substantially identical to that published previously and is reproduced here for the convenience of the reader.

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 which in the context of this article is the chemical synthesis of a compound from its elemental constituents. These, in turn, must first be dissolved in a fused salt solution from which they are extracted by the passage of electrical current. The principal components of an electrochemical cell are the electrolyte, the electrodes, and the container (sidewalls and floor). The electrolytes are multicomponent melts of either halides, chlorides or fluorides, or oxygen bearing anions, such as carbonates, molybdates, and tungstates.

During electrolysis electric current is passed from the anode through the electrolyte to the cathode. The electrolyte (or cell bath) must be strictly an ionic conductor, while the electrodes must be electronic conductors. The anode can be either consumable or nonconsumable. In electrosynthesis, the consumable anode may act as the feedstock for the deposited compound. In chloride electrolytes carbon commonly serves as a nonconsumable anode. There is no fully satisfactory nonconsumable anode for use with fluoride-based electrolytes. Recently, with reference to the Hall cell for the electrolytic extraction of aluminum a new approach to discovering nonconsumable anodes for use in fused salt electrolysis operations has been described along with the relevant set of selection criteria (2).

As for cathode materials, carbon, refractory metals such as tungsten, molybdenum, and tantalum, as well as low carbon steel have all been employed. In practice, the cathode functions only as the current lead and substrate for the deposit. During electrolysis the cathode element is coated by the product refractory metal compound.

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. Cell voltages depend upon the particular melt chemistry and cell design which determines the magnitude of the ohmic resistance of the bath. Current densities are in the neighborhood of 1 A cm^{-2} . Cell operating temperatures span 400° to 1000°C .

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. Voltage efficiency is defined as 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, e.g., the physical resistance of the electrolyte, the electrodes, bus bars, and contacts as well as overvoltages associated with the faradaic processes occurring at each electrode.

At least on the basis of reports in the open literature fused salt electroplating of refractory metal compounds has received little attention. The most thoroughly studied compounds are titanium diboride and tungsten carbide.

Coatings of titanium diboride have been deposited both to impart corrosion resistance against attack by liquid metal (3,4) and to offer abrasion resistance (5-9). More recently, investigators have begun studying the associated electrode processes (10). Generation of tungsten carbide coatings has been driven by the desire to form material for use in abrasion resistant coatings (11-14). Studies of electrochemical fundamentals have begun (15,16). Other refractory metal compounds whose electroynthesis has been reported include zirconium diboride (17), chromium boride (18), molybdenum disilicide (19), tantalum carbide (20) and molybdenum carbide (21). More recently, attention has turned to a broader array of materials syntheses, including metal matrix composites (22) and refractory-metal oxides containing controlled subvalent forms of the refractory-metal ion (23). In the case of the latter, electroynthesis from fused salts has facilitated the generation of compounds otherwise produced thermochemically at high temperatures and high pressures.

An alternative to electroynthesis 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, electroynthesis is a process for the faradaic discharge of both metal and oxygen (both 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 (24).

Cryogenic Electrolytes

As for cryogenic electrolytes, these 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 (25). Later in this article reference will be made to future prospects for electrochemical processing in these media.

Future Directions: Fused Salt Electrolysis

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, purity of product, corrosion of cell components, and 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 the cathode product. Furthermore, 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, 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 (26-28), or invent divided cells featuring staged reactions (29). The morphological problem has been attacked in some cases by adding leveling agents to the electrolyte. While potentially beneficial, their use

has been examined for refractory metal compounds.

Besides the structural problems associated with new electrolytic systems, the use of fused salt electrolysis must be taken into account. Care must be paid to the production of high quality products.

From the perspective of fused salt electrolysis, local advanced materials processing, etc., but it is difficult to generate the desired structures. Turbulent flow and nonequilibrium conditions in the electrolyte compositionally affect the refractory metal formation (31) and are restricted to regions in the literature that have been underexploited.

Earlier in this article the potential role of fused salt electrolysis in such media? It is not clear if it is able to electrochemically process refractory metals. Thirdly, the process must be controlled to achieve surface smoothing and it is said to have a high temperature processing problem. microcrystalline structures in cryogenic temperatures by low energy. The products are precisely controlled dimensions. Fused salt electrolysis is a gas at the outside of contaminants, albeit sparingly. Fused salt electrolytes are

of refractory metal compounds are titanium

has been examined only for electroplating of metal (30), but evidently not for electrosynthesis of compounds.

Besides the strictly technical issues there is a host of 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 nonelectrochemical synthesis processes, steps must be taken to design flowsheets with a minimum number of unit operations. More attention must be paid to environmental, health and safety issues. Care must be exercised to ensure that the production of the refractory metal compound be ecologically sound.

From the perspective of a technology capable of generating advanced materials, fused salt electrolysis looks extremely attractive. Again, its full potential has hardly been exploited. Advanced materials are characterized not only by their specialized chemistries, i.e., 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. Tungsten carbide powder has been synthesized by fused salt electrolysis (14). 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 metal compounds. Although there are reports in the literature of metastable phase formation (31) and deposition of single crystals with preferred orientation (32), these results were restricted to refractory metals and not their compounds. Among the layered structures reported in the literature is molybdenum carbide on diamond (33). Overall, this field is severely underexploited.

Future Directions: Cryogenic Electrolysis

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. Thus, in principle, one should be able to electrodeposit elements that cannot be plated from aqueous solutions. Secondly, the processing temperatures are very low with the result that thermal damage to the substrate is minimized. Thirdly, 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 nanoscale dimensions. Fourthly, the preparation of the electrolyte systems involves the condensation of a gas at the outset with the result that the solutions have the potential to be uncommonly free of contaminants. One of the drawbacks of high temperature electrolytes is that they 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 data base for these liquids is almost nonexistent cryoelectrodeposition has been conducted to date on an empirical basis to a large extent (34). Vital information such as compound solubilities and decomposition potentials, which are essential in describing the chemistry and electrochemistry of the process, is unreported. 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 nonaqueous electrochemistry has proven its viability in metallurgical processing in the opinion of this author the technological applications have not been exhausted. In particular, the electrosynthesis of refractory metal compounds shows great promise. New commercial development requires a more complete data base and more confidence in our ability to translate discovery into process and product. Scientific and technical problems remain to be solved before the full potential of this technology will be felt in the marketplace.

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