

THE GENERATION OF COATINGS AND THIN FILMS
OF REFRACTORY METALS
BY ELECTROLYSIS IN NONAQUEOUS MEDIA

Donald R. Sadoway

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Abstract

Electrochemical processing in nonaqueous media has an important role to play in the generation of coatings and in the synthesis of thin films of refractory metals and their compounds. These media offer processing conditions unavailable in aqueous electrolytes: 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 inaccessible in aqueous systems. As well, tailored microstructures, such as thin films, epitaxial layers, and nonequilibrium structures such as compositionally graded and compositionally modulated microstructures can be produced electrochemically. The characteristics of electrochemical processing in nonaqueous media are presented. The potential of electrochemical processing in nonaqueous media to generate technologically important products is assessed.

Introduction

This author has recently reviewed both the synthesis of refractory-metal compounds by electrochemical processing in nonaqueous media (1) and fused salt electrolysis of refractory metals (2). This article is substantially identical to those two previous publications and is included in this volume for the convenience of the reader.

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 conductivities of both TiB₂ 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 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.

Why, then, nonaqueous media for electrodeposition of refractory metals? 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. As well, organic electrolytes can have some or all of the following characteristics: low flash point, carcinogenic, and violently reactive with water.

The purpose of this article is to describe the theory and practice of fused salt electrolysis as it applies to the electrodeposition of coatings and thin films of refractory metals and their 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.

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 which in the context of this article is the deposition of a coating or thin film of a refractory metal or compound from solution. The elemental constituents of the deposit, in turn, must first be dissolved in the molten salt from which they are extracted by the passage of electrical current which drives faradaic processes at each electrode. 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 electrodeposition, the consumable anode may act as the feedstock for the deposit. 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 (3).

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 depend upon the nature of the cell product. Electrowinning cells for primary extraction of liquid metal, e.g., aluminum, magnesium and the alkali metals, operate in the neighborhood of 1 A cm^{-2} ; electroplating cells for deposition of solid metal run in the range of $10 - 100 \text{ mA cm}^{-2}$. 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.

Fused salt electroplating of refractory metals has been studied for many years, although the level of effort appears to have dropped off in the last decade. The following citations are representative of the more recent literature. The most thoroughly studied metals are molybdenum (4-7) and titanium (8,9). Other metals, however, continue to receive attention: niobium (10,11), tantalum (10, 12, 13), chromium (14-17), and tungsten (18). Electrodeposited coatings can be pure metal, metal alloy, or compounds. Reports of research on the electrodeposition of alloys include Mo-Nb (19), Ni-Ta (20) and Ni-Nb (20).

As for electrodeposition of compounds containing refractory metals, the earliest work was concentrated on the production of carbides, primarily for the purposes of generating abrasion resistant coatings (18, 21). Over time the focus of electrodeposition of compounds has changed to include a wide range of chemistries. Coatings of titanium diboride have been deposited both to impart corrosion resistance against attack by liquid metal (22, 23) and to offer abrasion resistance (24-28). More recently, investigators have begun studying the associated electrode processes (29). Generation of tungsten carbide coatings has been driven by the desire to form material for use in abrasion resistant coatings (30, 32, 33). Studies of electrochemical fundamentals have begun (34, 35). Other refractory metal compounds whose electrosynthesis has been reported include zirconium diboride (36), chromium boride (37), molybdenum disilicide (38), tantalum carbide (39) and molybdenum carbide (40). More recently, attention has turned to a broader array of materials syntheses, including metal matrix composites (41) and refractory-metal oxides containing controlled subvalent forms of the refractory-metal ion (42). In the case of the latter, electrosynthesis from fused salts has facilitated the generation of coatings of compounds otherwise produced thermochemically at high temperatures and high pressures.

Another way to generate coatings and thin films of refractory-metal oxide compounds is anodization. The distinction between the anodization and electrosynthesis 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 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 (43).

Cryogenic Electrolytes

Cryogenic electrolytes do not appear in contemporary metallurgical technology. Electroplating of elemental refractory metal (44) and electrosynthesis of compounds containing refractory metals (31), both processes conducted in subambient and cryogenic liquids, have been reported, but not at the commercial scale. 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 (45-47), or invent divided cells featuring staged reactions (48). The morphological problem has been attacked in some cases by adding leveling agents to the electrolyte. While potentially beneficial, their use has been examined only for electroplating of metal (49), 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 deposition 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.

From the perspective of a technology capable of generating advanced materials, fused salt electrolysis looks extremely attractive. 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, including 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 and their compounds. There are reports in the literature of metastable phase formation (50) and deposition of single crystals with preferred orientation (51), both restricted to refractory metals and not their compounds. Among the layered structures reported in the literature is molybdenum carbide on diamond (52). 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 electrodeposition of coatings and thin films of refractory metals? 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. This can lead to contamination of the electrodeposits if such dissolution products are electrochemically active. In contrast, processing at low temperatures can avoid this; and so, when high purity is a concern, cryogenic electrolytes are excellent processing media. Finally, there is the question of space/time yield. When compared with other electrodeposition processes, cryoelectrodeposition is very slow. Current densities on the order of $1 \mu\text{A cm}^{-2}$ are not uncommon. However, this represents high productivity when compared with growth rates for films generated by vapor phase processes. The low solute solubilities in cryogenic liquids (and hence low limiting current densities) are compensated by the much higher density of matter in the liquid state than in the vapor phase.

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. 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 electrodeposition of coatings and thin films of refractory metals and their 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.

References

1. D.R. Sadoway, "The Synthesis of Refractory-Metal Compounds by Electrochemical Processing in Nonaqueous Media," in Refractory Metals: Extraction, Processing, and Applications, K.C. Liddell, R.G. Bautista and D.R. Sadoway, editors, (Warrendale, PA: TMS, 1991), 8 pp.
2. D.R. Sadoway, "Fused Salt Electrolysis of Refractory Metals," in Refractory Metals: State-of-the-Art 1988, P. Kumar and R.L. Ammon, editors, (Warrendale, PA: TMS, 1989), 155-165.
3. D.R. Sadoway, "A Materials Systems Approach to Selection and Testing of Nonconsumable Anodes for the Hall Cell," in Light Metals 1990, C.A. Bickert, editor, (Warrendale, PA: TMS, 1990), 403-407.
4. G.J. Kipouros and D.R. Sadoway, "The electrodeposition of improved molybdenum coatings from molten salts by the use of electrolyte additives," J. Appl. Electrochem., 18 (6) (1988), 823-830.
5. V.I. Shapoval, A.N. Baraboshkin, Kh.B. Kushkhov, and V.V. Malyshev, "Specific features of the electroreduction of MoO_3 forms in the presence of a tungstate melt," Elektrokhimiya, 23 (7) (1987), 942-946.
6. K. Koyama, Y. Hashimoto, and K. Terawaki, "Smooth electrodeposits of molybdenum from $\text{KF} - \text{K}_2\text{B}_4\text{O}_7 - \text{K}_2\text{MoO}_4$ fused salt melts," J. Less-Common Met., 134 (1) (1987), 141-151.
7. T. Hatusika, M. Miyake, and T. Suzuki, "Formation of refractory metal films in low temperature molten salt bath," Kenkyu Hokoku - Asahi Garasu Kogyo Gijutsu Shoreikai, 49 (1986), 289-293.
8. X. Gu, S. Duan, and D. Inman, "Electroplating of titanium in molten $\text{LiCl} - \text{KCl}$ eutectic containing lower-valent titanium," Xiyou Jinshu, 7 (3) (1988), 182-186.
9. A. Robin, J. De Lepinay, and M.J. Barbier, "Electrolytic coating of titanium onto iron and nickel electrodes in the molten $\text{LiF} + \text{NaF} + \text{KF}$ eutectic," J. Electroanal. Chem. Interfacial Electrochem., 230 (1-2) (1987), 125-141.
10. P. Taxil and J. Mahenc, "Formation of corrosion-resistant layers by electrodeposition of refractory metals or by alloy electrowinning in molten fluorides," J. Appl. Electrochem., 17 (2) (1987), 261-269.
11. G.P. Capsimalis, E.S. Chen, R.E. Peterson, and I. Ahmad, "On the electrodeposition and characterization of niobium from fused fluoride electrolytes," J. Appl. Electrochem., 17 (2) (1987), 253-260.
12. A.W. Berger, "Fused-salt electrodeposited tantalum coatings," Chem.-Anlagen Verfahren, no. 3: 1980, 82-84.
13. P. Los, J. Josiak, A. Bogacz, and W. Szklarski, "Tantalum coatings deposition from fluoride electrolytes," Arch. Hutn., 29 (4) (1984), 515-527.
14. T. Vargas, R. Varma, and A. Brown, "Electrodeposition of microcrystalline chromium from fused salts," in Molten Salts, ECS Symposium Vol. 87-7, ed. G. Mamantov, M. Blander, C. Hussey, C. Mamantov, M.-L. Saboungi and J. Wilkes (Pennington NJ: The Electrochemical Society, 1987), 1018-1027.
15. A.M. Emsley and M.P. Hill, "The corrosion and deposition performance of molten salt electrodeposited chromium coatings," J. Appl. Electrochem., 17 (2) (1987), 283-293.
16. T. Vargas and D. Inman, "Controlled nucleation and growth in chromium electroplating from $\text{LiCl} - \text{KCl}$ melt," J. Appl. Electrochem., 17 (2) (1987), 270-282.
17. R.A. Bailey and T. Yoko, "High-temperature electroplating of chromium from molten FLINAK," J. Appl. Electrochem., 16 (5) (1986), 737-744.
18. H. Yabe, Y. Ito, K. Ema, and J. Oishi, "Electrodeposition of tungsten and tungsten carbide from molten halide," in Molten Salts, ECS Symposium Vol. 87-7, ed. G. Mamantov, M. Blander, C. Hussey, C. Mamantov, M.L. Saboungi and J. Wilkes (Pennington NJ: The Electrochemical Society, 1987), 804-813.
19. Z.I. Valeev, A.N. Baraboshkin, Z.S. Martem'yanova, and N.O. Esina, "Electrodeposition of molybdenum -niobium alloys from their chloride melt," Elektrokhimiya, 24 (1) (1988), 59-63.
20. Z. Qiao and P. Taxil, "Electrochemical surface alloying on nickel with tantalum and niobium in molten fluorides and properties of tantalum - nickel and niobium - nickel alloys," Jinshu Xuebao, 23 (2) (1987), B76-B83.
21. K.H. Stern and S.T. Gadomski, "Electrodeposition of tantalum carbide coatings from molten salts," J. Electrochem. Soc., 130 (2) (1983), 300-305.
22. K. Matiasovsky, K. Grjotheim and M. Makyta, "Electrolytic deposition of titanium diboride - possible impact on aluminum electrolysis," Metall (Berlin), 42 (12) (1988), 1196, 1198-1200.
23. D.W. Townsend and L.G. Boxall, "Titanium diboride coatings prepared by plasma spraying and electroplating," in Light Metals 1984, (Warrendale, PA: TMS, 1984), 555-571.
24. W.S. Ricci, J.L. Wong, M. Levy and K.J. Bhansali, "Fused salt electrodeposited titanium boride coatings on high speed steel twist drills," Report MLT-TR-87-48, 1987, 25 pp., Chem. Abs. 109 (20): 174183w.
25. S. Nishikida and F. Matsuno, inventors, Sumitomo Metal Industries, Ltd., assignee, "Ceramic coatings on steels," Japanese patent, no. 62,112,782 A2, May 23, 1987.

26. A. Bogacz, P. Los, W. Szklarski and J. Josiak, "Electrolytic preparation of titanium boride and lanthanum boride," Rudy Met. Niezelaz., 28 (4) (1982), 134-139.
27. D.R. Flinn, F.X. McCawley, G.R. Smith and P.B. Needham, Jr., "Electrodeposition of erosion-resistant titanium diboride coatings," U.S. Bureau of Mines Rep. Invest., RI 8332, 1979, 29 pp.
28. J.D. Kellner, inventor, United Aircraft Corp., assignee, "Electrodepositing titanium diboride from fused salts," U.S. patent, no. 3,880,729, April 29, 1975.
29. M. Makyta, K. Matiasovsky and V.I. Taranenko, "Mechanism of the cathode process in the electrochemical synthesis of titanium boride in molten salts - I. The synthesis in an all-fluoride electrolyte," Electrochim. Acta, 34 (6) (1989), 861-866.
30. Kh.B. Kushkhov, I.A. Novoselova, D.G. Supatashvili and V.I. Shapoval, "Coelectroreduction of fluorine oxide complexes of tungsten and carbon dioxide in a chloride-fluoride melt," Elektrokimiya, 26 (1) (1990), 48-51.
31. D.F. Sadoway and R.M. Rose, inventors, Massachusetts Institute of Technology, assignee, "Cryoelectrosynthesis," U.S. patent, no. 4,971,663, November 20, 1990.
32. K.H. Stern and M.L. Deanhardt, "Electroplating of tungsten carbide from molten fluorides," J. Electrochem. Soc., 132 (8) (1985), 1891-1895.
33. V.I. Shapoval, Kh.B. Kushkhov and I.A. Novoselova, "High temperature electrochemical synthesis of tungsten carbide," Zh. Prikl. Khim. (Leningrad), 58 (5) (1985), 1027-1030.
34. H. Yabe, K. Ema and Y. Ito, "The effect of silver ion on electrodeposition of tungsten and tungsten carbide from molten chloride," Electrochim. Acta, 35 (1) (1990), 187-189.
35. B. Hofman and H. Scholl, "Voltammetry of mixed tungsten-titanium carbide in nonaqueous and mixed solvents," Elektrokimiya, 24 (9) (1988), 1264-1267.
36. J.M. Gomes and K. Uchida, inventors, U.S. Dept. of the Interior, assignee, "Electrolytic preparation of titanium and zirconium diborides using a molten, sodium salt electrolyte," U.S. patent, no. 3,775,271, November 27, 1973.
37. T. Arai and Y. Sugimoto, inventors, Toyota Central Research and Development Laboratories, Inc., assignee, "Formation of carbide or boride coatings of Group VB metals or chromium on carbon product surface," Japanese patent, no. 52,029,500, March 5, 1977.
38. N. Petrescu, M. Petrescu, M. Britchi and L. Pavel, "Silicide coatings on molybdenum obtained by electrotransport and diffusion from molten fluorides," Rev. Roum. Chim., 18 (11) (1973), 1853-1858.
39. K.H. Stern and S.T. Gadomski, "Electrodeposition of tantalum carbide coatings from molten salts," Rev. Int. Hautes Temp. Refract., 24 (2) (1987), 71-83.
40. V.I. Shapoval, Kh.B. Kushkhov, V.V. Malyshev, P.V. Nazarenko and N.P. Baydan, "The properties of molybdenum carbide coatings on different materials," Zashch. Met., 4 (1986) 564-566.
41. G.A. Hope and R. Varma, "Molten salt deposition of metal matrix composite materials," Aust. J. Chem., 41 (8) (1988), 1257-1259.
42. M.E. De Roy and J.P. Besse, "Synthesis of single-crystal inorganic compounds by electrochemical reduction in a molten medium," Rev. Int. Hautes Temp. Refract., 24 (2) (1987), 71-83.
43. V.P. Yurinskii, E.G. Firsova, A.G. Morachevskii, and A.A. Maiorov, "Mechanism and kinetics of the electrochemical oxidation of molybdenum and tungsten in molten alkali metal nitrates," Zh. Prikl. Khim. (Leningrad), 57 (3) (1984), 695-698.
44. R.M. Rose and D.R. Sadoway, "Cryoelectrodeposition," U.S. patent, no. 4,517,253, May 14, 1985.
45. Sony Corp., assignee, "Diaphragm for fused salt electrolysis," Japanese patent, no. 56/5832 [81/5832], Feb. 6, 1981.
46. E. Chassaing, F. Basile, and G. Lorthioir, "Fused-salt electrolysis for production of titanium metal - present state and future developments," in Titanium '80 Science and Technology, H. Kimura and O. Izumi, editors, (Warrendale, PA: TMS-AIME, 1980), 1963-1967.
47. G. Cobel, J. Fisher, and L.E. Snyder, "Electrowinning of titanium from titanium tetrachloride: pilot plant experience and production plant projections," in Titanium '80 Science and Technology, H. Kimura and O. Izumi, editors, (Warrendale, PA: TMS-AIME, 1980), 1969-1976.
48. M.V. Ginatta, private communication, "Industrial plant for the production of electrolytic titanium, Ginatta technology," report RT 88-03-077, Ginatta S.A., Torino, Italy, March 1988.
49. G.J. Kipouros and D.R. Sadoway, "The electrodeposition of improved molybdenum coatings from molten salts by the use of electrolyte additives," J. Appl. Electrochem., 18 (6) (1988), 823-830.
50. K.A. Kaliev, A.N. Baraboshkin, and S.M. Zakhar'yash, "Formation of metastable phases during the electrolysis of Na_2WO_4 - Li_2WO_4 - WO_3 system melts," Elektrokimiya, 20 (3) (1984), 328-331.
51. A.N. Baraboshkin, Z.S. Martem'yanova, S.V. Plaksin, and N.O. Esina, "Preferred orientation of the growth of metals electroplated from fused salts. Relation between crystal habit and direction of the orientation axis," Elektrokimiya, 14 (1) (1978), 9-15.

52. V.I. Shapoval, Kh.B. Kushkhov, V.V. Malyshev, V.T. Vesna and V.P. Maslov, "Deposition of molybdenum carbide on the surface of diamonds by electrolysis of ionic melts," Poroshk. Metall., (7) (1986), 43-45.