

REVIEW

Electrocoating from molten salts*

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Received 3 April 1978

Electrolytic deposition processes from molten salt baths, i.e. metallizing and electroplating, for coating metal or alloy substrates are described. An outline of the general experimental techniques employed in molten salts and the influence of various factors such as impurities, cation valency, nature of the solvent, stability of complex ions, temperature, current density, kinetics, and additives, on the electrolytic processes are discussed. A review of the current status of electrodeposited coatings from molten salts, with special reference to diffusion coatings on metal and alloy surfaces, is presented. The available physical, chemical, and mechanical properties of the coatings thus formed and their applications are summarized. Some suggestions are made to show the directions in which further research in this field is necessary.

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1. Introduction

Metallic coating and/or alloying is an effective means for the improvement of resistance of metals to attack by corrosive environments at either ordinary or elevated temperatures. Metallic coatings obtained by conventional methods, e.g. by electroplating in aqueous solutions, commonly have flaws such as pinholes (porosity) and are susceptible to pitting of the underlying metal layers by galvanic action. To overcome this problem thicker metallic coatings are often employed. On the other hand, a thinner coating obtained by an electrolytic molten salt process, e.g. metallizing [1] can do the same job since the coatings obtained by this process are very uniform and non-porous owing to the diffusion of atoms of one metal into the surface of another. The diffused metal becomes an integral part of the surface of the other metal, instead of being just mechanically attached to the surface as in con-

* This review was reproduced from the Proceedings of the International Conference on Advances in Surface Coatings Technology, published by the Welding Institute.

ventional plating. The alloy coatings can generally be formed with a high degree of electrolytic efficiency and an unusual degree of thickness control. This is subject to the fundamental condition of solid solution or intermetallic compound formation [2, 3] between the two reacting surfaces.

Electrolytic metal plating in molten salts has a number of other advantages compared with electroplating in aqueous solutions. These include: a higher efficiency of the electrolysis (occasionally by an order of magnitude [4]); often high deposition rates; a better 'throwing power' (or ability to plate uniformly over an intricate surface) [4–6]; better anticorrosion properties of the deposited metal [4]; layers free of stress so that a plated part can later be deformed [7]; and applicability to a wide range of metal substrates. In comparison with hot dipping and gas or pack cementation processes, electrolytic cementation from molten salts (metalliding) has the possible advantage of independent control [8–14] over the rate of metal deposition (by changing the cathode current density) and the rate of metal diffusion into the substrate (by changing the temperature). This should provide economies of metal.

The electrolytic process for the production of aluminium, magnesium, and sodium from molten salt baths are well known [15]. Melts are now available for the electroplating of a variety of elements: metals that cannot be electrodeposited from aqueous solutions, e.g. Nb, Ta, Ti, Zr, Mo, W [16–22], Al [23–26], etc.; some traditional materials that may be plated with far higher deposition rates [4] than in aqueous electrolytes, i.e. Sn and Zn; some metals that can be deposited only in aqueous electrolytes in limited thickness [7], e.g. Pt, Pd, Rh, Ir, Ru; for making surface alloys [1, 8] and for electroforming refractory [27, 28] and platinum group [29, 30] metals.

A wide variety of hardfacing materials on base metal substrates is used nowadays for a large number of industrial applications [31]. Those hardfacing materials are generally produced on the base substrate either by welding the hardfacing material to the substrate or by treating the base substrate in such a manner as to harden its surface. Electroplating from molten salts appears to be a very promising way of surface finishing,

both with respect to protection against corrosion, high temperature oxidation and/or to the possibility of obtaining very hard surfaces with special mechanical properties. However, in most situations the technical application of electrocoating from molten salts involves the solution of some fundamental problems of both theoretical and technical kinds. These include: composition and structure of the electrolyte, e.g. anionic and cationic [17, 22], of the underlayer and of the deposited metallic layer [32–38]; fundamental thermodynamic information, e.g. e.m.f. series [39]; electrode reaction mechanisms [17, 18, 40–46]; optimum design factors [21], e.g. plating cell, electrodes, etc.; effect of impurities; optimum processing parameters and general experimental techniques.

In this review, some of these factors will be highlighted and the literature data on electrocoating processes from fused salts of major significance will be surveyed.

2. Electrolytic metal coating processes from molten salts

There are two main electrolytic deposition processes for coating metal or alloy substrates from molten salts. These are: metalliding, which produces a metallic coating diffused into the substrate, and electroplating, which produces a non-diffused, continuous, and coherent metal coating on the substrate. The former process has also been referred to as electrolytic cementation [47] because of its close resemblance to the pack-cementation process (both are substrate-dependent). A brief description of the two processes and their salient features is given below.

2.1. *The metalliding process*

Metalliding is a molten salt electrolytic process whereby metal ions can be driven into a surface to produce diffusion coatings (surface alloys) in a very controlled manner [1]. A metalliding metal (the metal to be deposited) is employed as the anode and the cathode is the metal or metal article upon which the coating is to be applied. Most of the metalliding reactions involve the diffusion of more reactive metals (anode) into less reactive metals (cathode) and consequently

the system constitutes a galvanic cell or battery. When the metallizing anode is externally shorted to the cathode, electrons flow from anode to the cathode. Under these conditions the metallizing metal dissolves in the fused salt bath and metallizing ions are discharged at the surface of the metal cathode, where they form a deposit which immediately diffuses into and reacts with the metal to give a metallide or diffusion coating. The rate of dissolution and deposition of the metallizing agent is self-regulating in that the rate of deposition is equal to the rate of diffusion of the metallizing metal into the cathode substrate.

Most metallizing reactions will sustain themselves through the battery action of the internally generated e.m.f. In practice, however, an external voltage is usually superimposed on the internal e.m.f. to achieve a more uniform and higher current density than the battery action will provide. In this way, metallizing has been reported [12, 13] to proceed from 3–10 times faster than with the self-generating battery action without exceeding the rate at which the alloying agent can diffuse into the cathode substrate. The deposition rate, therefore, can be controlled (increased or decreased) either by an applied external e.m.f. or by inserting a variable resistance in the circuit.

Molten alkali and alkaline earth fluorides serve as the electrolyte. The process is operated at between 500° C and 1100° C in inert atmospheres and in metal vessels. The throwing power of the fluoride bath is good [27, 48] and the shape of the article to be metallized is unimportant. The alloy coatings are generally uniform, non-porous, and with no edge build-up [12]. These may consist of solid solutions, inter-metallic compounds, or mixtures of solutions and compounds. In most instances a major part of the surface layer will consist of the particular compound that is most stable under the conditions of deposition.

An additional feature of metallizing is that the molten fluorides dissolve oxide layers from metal surfaces. These oxides act as barriers in metal diffusion processes. This largely accounts for the rapid diffusion rates encountered in many metallizing reactions. It has been reported [41, 49] that under cathodic conditions oxide layers are totally removed. This is rarely so in non-

electrolytic methods, even those employing high temperatures.

2.1.1. Metallizing reactions. The various metals in contact with their molten, solid, or gaseous fluorides can be arranged in the form of an e.m.f. series in decreasing order of their reactivity based on the free energy of the formation of the fluoride. The practical difficulties of compiling a reliable series based on experimental measurements in different fluoride melts have been pointed out [50]. A theoretical e.m.f. series has been compiled by the present author [39] from the recently available thermodynamic and thermochemical data. The method of calculations has been discussed in a previous paper [51]. A shorter version of the series is presented in Table 1. The position of an element in this series offers a rough guide in predicting the metallizing reactions. The higher the position of any element in the series, the more electrochemically reactive is the element, and the more able it is to form a diffusion coating on any element below it in the series, provided they are mutually soluble or form a compound [2, 3].

Table 1. Theoretical standard e.m.f. of metal-fluorine couples with molten fluoride electrolyte

Metal	Fluoride	e.m.f. (V) at		
		600° C	800° C	1000° C
Sr	SrF ₂	5.520	5.367	5.211
Ca	CaF ₂	5.520	5.355	5.184
Ba	BaF ₂	5.448	5.293	5.139
Li	LiF	5.455	5.256	5.069
Y	YF ₃	5.067	4.929	4.797
Zr	ZrF ₄	4.164	4.020	3.933
Al	AlF ₃	3.973	3.813	3.653
Be	BeF ₂	3.968	3.785	3.628 (4.073)*
Si	SiF ₄	3.702	3.628	3.554
Mn	MnF ₂	3.496	(3.369)	3.254
Cr	CrF ₂	3.325	3.197	3.074
Cr	CrF ₃	3.191	3.053	2.919
Ta	TaF ₅	2.740	2.690	2.642
Co	CoF ₂	2.772	2.636	2.505
Ni	NiF ₂	2.714	2.558	2.573
Rh	RhF ₄	1.824	1.725	1.668
Pt	PtF ₄	1.426	1.330	1.266
Pt	PtF ₃	1.311	1.179	1.069

* Values in parentheses are estimated

Metals that are more reactive than the anode metal, i.e. higher up in the e.m.f. series, can often be metallided if the activities of the metals are not too far apart and if the alloying agent diffuses rapidly into the cathode and lowers its activity. This is the situation in aluminiding zirconium and hafnium, and berylliding yttrium.

When metalliding against the e.m.f. series [39] a fairly high negative voltage is usually applied to the sample as it is immersed, and the voltage is not removed until the sample is taken out of the molten salt.

2.1.2. Extension of the metalliding process.

Double metalliding offers a multitude of sequentially or simultaneously formed double-alloy coatings with great potential as wear- and corrosion-resistant surfaces. For example, chromiding borided steel. In these examples it is important to obtain uniformly diffused coatings, otherwise one of the benefits may be lost.

2.2. Electroplating process

The expression 'fused salt electroplating' is too often used for processes which are better described as 'electrolytic cementation'. To avoid confusion it is important to distinguish between diffusion coatings (metallided coatings) and 'true' electroplated coatings. A true electroplated coating [16] has the following characteristics:

(a) The composition of electroplated coating is constant through the thickness of the coating.

(b) Its rate of deposition is determined by the current, is limited by the diffusion rate of ions in the liquid electrolyte, and is independent of the substrate or rates of solid-state diffusion (cf. metalliding: rate of diffusion of the metallided element into the substrate is effectively the rate-controlling process; this rate diminishes as metalliding proceeds and further treatment may yield only a low quality surface deposit).

(c) In principle, there is no thickness limit for electroplating although slowly increasing roughness with thickness may impose a practical limit.

In the past the electrolysis of molten salts, in the absence of subsequent diffusion alloying,

has usually resulted in the production of compact powders or adherent dendritic deposits. However, in recent years a significant number of papers have reported the production of pure electroplate on a number of metal substrates.

2.2.1. Extension of electroplating process.

Electroforming is a process in which an object of simple or complex shape can be produced by electroplating on a substrate and the substrate is then usually removed by dissolution with a suitable acid. Electroformed articles of refractory metals [5, 16, 27] and platinum metals [7, 29, 30] from molten salts have been reported.

3. General experimental procedures

There are only two main studies for electro-coating metals from molten salts for which any systematic general experimental information is available. These are metalliding and electroplating with refractory metals. Although the optimum operating parameters for the deposition of the metals and alloys are not identical, they are, nevertheless, sufficiently similar for a detailed general description to serve for both processes.

Experimental techniques in molten fluorides have been recently reviewed by Bamberger [52]. The standard general procedure and usual precautions necessary for the preparation of molten salt baths must be followed [13, 14, 17, 41, 48, 53-56]. Some of the specific conditions which will be cited in connection with metalliding in the forthcoming description have been suggested by Cook [1, 12, 13, 57], who has done most of the earlier work in this field. Conditions for the electroplated coatings of refractory metals are, in general, those suggested by Mellors and Senderoff [5, 16, 17]. Needless to say, these conditions will have to be modified to suit individual requirements.

3.1. Solvent and solute compositions

Four main classes of baths have been successfully employed for electrolytic metal plating from melts. These are molten:

(a) fluoride solvents, i.e. LiF-NaF-KF (melting point 454° C), LiF-NaF (melting point 650° C),

NaF–KF (melting point 710° C), LiF (melting point 850° C), etc.

(b) chloride solvents, i.e. LiCl–NaCl, NaCl–KCl, AlCl₃–NaCl–KCl, SnCl₂–KCl, ZnCl₂–KCl, etc.

(c) cyanide solvents, i.e. NaCN, KCN, NaCN–KCN

(d) salt solvents containing oxygen, i.e. borates–titanates, CaCl₂–CaWO₄, etc.

Of these four types of melt only fluorides have been used for the deposition of a large number of elements, i.e. refractory metals and for metalliding. Recently, molten cyanides have been reported to be very successful [7, 30] for the deposition of the platinum group of metals. Chlorides are also finding application for electroplating with aluminium, tin, and zinc [4]. The use of oxygen-containing compounds, for instance CaWO₄, is limited to very special applications.

For the metalliding process a solute concentration about 0.01–5 mol% fluoride of the metal to be deposited is favourable. Higher concentrations of solutes, up to ~ 50 mol%, are employed in certain instances when metalliding with yttrium and rare earths, or when the sequential or simultaneous diffusion of two metals is required. The preferred operating temperature range is between 900° C and 1100° C.

For the electrodeposition of refractory metals a solute concentration about 10–15 wt% simple or complex fluoride of the refractory metal, e.g. ZrF₄ or K₂TaF₇, in a mixture of alkali fluoride, e.g. LiF–NaF–KF, is generally employed. The temperature employed is between 700° C and 850° C.

3.2. Containers and electrodes

Some general information on the design of plating cells and electrode geometry is available [13, 14, 21, 52] but this has to be modified to suit individual requirements.

Glass or quartz can be used only for chlorides but cannot be used to contain fluoride melts for long-term experiments, since small traces of moisture will result in the formation of HF and attack the containers. The most common materials for containing molten fluorides are steel, nickel alloys, e.g. Inconel, Monel, high density grade graphite, or vitreous carbon. However, possible

interactions with the solute and the effect of stray electrical potentials, resulting in anodic dissolution must be considered when using metallic containers.

In a typical laboratory experiment the alkali fluoride salt mixture is contained in an appropriate crucible which is then placed in a suitable metal or alloy cell. The cell is usually flanged at the upper end and covered with a water-cooling plate. Above this plate is the cell top plate containing a number of holes for the entry of electrodes, thermocouple tube, inert gas, and vacuum connectors. The cell is then placed in an electric furnace to heat and melt the salt. The metalliding experiments have been reported to be carried out at up to a 10 kg scale [57] and electroplating up to a 1500 kg scale [16].

Anodes are usually of the metal or the alloy to be deposited, either in sheet form or in certain circumstances as discrete pieces held in a porous metal or graphite basket.

3.3. Electrolytic characteristics of the processes

In metalliding the preferred range of current densities lies between 50 and 500 A m⁻², the applied voltage between 0.1 and 0.5 V. For plating refractory metals current densities between 50 and 1250 A m⁻², depending upon the geometry of the cathode and the metal being deposited, with an applied voltage between 0.1 and 0.25 V, have been suggested. Metal concentration, current density, and temperature are interrelated as is also the case in aqueous electroplating.

3.4. Purity considerations

3.4.1. The electrolyte. The chemical composition of the fused salt is important if good metallic coatings are to be obtained. The most common impurities present are: oxides, sulphates, silicates, iron, nickel, and carbon. The fluoride melts can be purified [52, 53, 56, 58] by a number of chemical and electrochemical treatments depending upon the type of impurities present. The electrocoating experiments should be carried out in an inert gas atmosphere, e.g. argon, nitrogen, forming gas, or under vacuum. A detailed account of the effect of impurities on the electrodeposits is given in Section 4.1.

3.4.2. Purity checks. Electrochemical techniques can be employed to check the purity of the melts [41, 53, 54, 59]. Galvanostatic and potentiostatic methods are commonly used; a general description of these methods is available in the literature [60–62].

4. Influence of various factors on the electrolytic deposition processes and the quality of coatings

It is very difficult to generalize the effect of various experimental parameters on the quality of the electrodeposited metal coatings obtained from fused salts. This is due to the lack of detailed information in the available literature and the proprietary nature of salt baths. The general discussion which follows in this section is mainly applicable to the electrodeposition of refractory metal coatings from molten fluorides unless stated otherwise.

4.1. Effect of impurities

The purer the electrodeposited metal the more ductile will be the coating. The microhardness of an electrodeposited metal is usually a sensitive indicator of its purity. This has been demonstrated [5, 20, 32] in electrodeposited niobium, titanium, chromium, etc.

4.1.1. Inorganic impurities. Anionic impurities such as oxide, hydroxide, chloride, bromide, and iodide have been found undesirable to different extents, depending upon the amount of impurity, type of melt, and the metal being electrodeposited. The presence of appreciable quantities of oxide and hydroxide ions in the melt produces hard and brittle deposits [5]. Atmospheric nitrogen dissolves in the melt and can produce a similar effect. For example, a typical coating of niobium [5] containing 0.001% N, 0.039% O, and 0.003% H had a hardness of 93 DPH, whereas another sample containing only < 0.0005% N, 0.021% O, and 0.0005% H had a DPH hardness value of 70.

Oxygen dissolved in the chloride melts has a similar effect [32]. The chlorides of the metals being deposited form oxychlorides such as VOCl_3 , CrOCl_2 , CrOCl , etc. These in turn form VO^{3+} ,

CrO^+ and other cations. Subsequent reduction of the cations at the cathode introduces oxygen into the electrodeposit.

Chlorides, bromides, and iodides have a variable effect depending upon the nature of the coating metal. Tantalum and niobium, for example [5, 28], can tolerate chloride ions up to 10 wt% before serious loss of coherence of the plate. Zirconium, on the other hand, can tolerate only small quantities of chloride ions. Fluoride ions present in the alkali chloride melts produce a similar effect in electroplating [32, 63], but a beneficial effect in metallizing has been recently reported [64]. However, as is very common in electrodeposition processes, traces of some of these impurities can show a beneficial addition agent effect; for example, by reduction of the grain size of the deposited metal, i.e. niobium [5].

It is also possible to contaminate the deposited metal coating with other metal impurities present in the anode material or the melt. The more electronegative metals such as aluminium, iron, etc., may pass into the melt from the anode, consequently these may be transferred to the deposited metal as a solid solution or an inter-metallic compound.

Most of the high melting metals are known to react and form compounds with B, C, Si, P, and S. It has been reported [32, 65] that these compounds are more electropositive and do not take part in the anodic reactions. These elements, therefore, are deposited only in negligible quantities and appear to have no effect on the deposition and quality of the metal.

During the electrodeposition process some refining of the impure anode material employed has been reported [5] with respect to carbon, oxygen, nitrogen, and tantalum, but not with respect to chromium. The reduction in carbon and oxygen is owing to their apparent loss by precipitation from the melt. The final impurity content of the cathode should be equal to or less than that of the anode.

4.1.2. Organic impurities. The carbon impurity in the bath is usually produced from the organic materials present in the salts. The fine carbon particles in the bath cannot be tolerated because they collect on the surfaces of the cathodes and can completely stop the electrolytic process in

some instances and produce inferior coating in others [13]. Methods are available for removing these impurities [48].

4.2. Valency of the cation

To achieve a good cathode current efficiency for the deposition of refractory metals the average valency for each of the metals in the solution must be close to a preferred average value. These are [17]: 3+ for Mo, Cr, V; 4+ for Nb, Zr, Hf; 4.5+ for W; and 5+ for Ta. If the valence is too high, poor efficiency and bad deposits will result.

The solute cations can also interact with solvent to form complex ions, e.g. $(\text{TaF}_7)^{2-}$, $(\text{NbF}_7)^{2-}$, $(\text{BF}_4)^{1-}$, $(\text{SiF}_6)^{3-}$, $(\text{AlF}_6)^{3-}$. The success of all-fluoride baths for plating can be considered to some extent to be associated with the marked stability of the fluoro-complexes of the metals. A comparable situation in aqueous systems is the use of cyanide electrolytes for the deposition of certain metals. The depositing metal cation forms a cyanide complex which slows down the rate of the deposition process so that a smooth, dendrite-free deposit is obtained, although surface effects are also important. It seems very likely that such a mechanism is also operative in the electro-deposition of platinum metals from molten cyanides [7, 29, 30].

4.3. Nature of the solvent/stability of complex ions

The stability of complex ions in alkali halide melts is strongly dependent on the nature of the solvent cation. Melts containing potassium ions have been observed [17] to produce more stable complexes compared with those containing sodium or lithium ions. Stability of complex ions must, therefore, be taken into consideration when comparing the properties of different plating baths. A semi-quantitative method for making these comparisons has been devised by Mellors and Senderoff [5].

4.4. Temperature of the bath

The temperature at which the process is conducted is dependent to some extent upon the particular fused salt bath employed. At the low end it is limited by the melting point of the salt mixture

and at the high end by the gradual loss of coherence of the deposit once a critical temperature is exceeded. The latter effect is probably associated with the increased dissociation of the fluoro-complexes at the higher temperatures. In metallizing an increase in temperature shortens the time of operation: usually a 100° C rise will give a two- to tenfold increase in diffusion rate..

4.5. Effect of current density

The preferred current density ranges for the metallizing and refractory metal plating have been mentioned earlier. In plating, the lower limit of the current density range is decided by the amount of the less electropositive metals (for instance Fe) present in the bath: the higher the amount, the higher the current density must be to minimize contamination of the deposit. The upper limit for current density increases with temperature and the depositing metal ion concentration until the diffusion limited current is reached; above this value alkali metal is deposited with disastrous results [17].

4.6. Kinetic factors

The influence of kinetic factors on the electro-deposition processes from molten salts has been discussed recently by Inman *et al.* [21, 40, 42] and others [17, 66]. The importance of nucleation overvoltages/surface phenomena [17, 33–35], the structure of the electrical double layer and specific anionic effects [42, 67] have also been emphasized.

Mellors and Senderoff [5, 68] have reported that the special property of fluoride melts which results in coherent plating, compared to the particulate deposits in other melts, is caused by the development of polarization because of an irreversible step in the cathodic reduction to metal. This step may result from the formation of an insoluble intermediate product on the electrode [68, 69], a corrosion phenomenon [63], or a slow chemical dissociation preceding the electro-chemical reduction [70].

4.7. Effect of additives

To study the effect of additives it is important

to study the parameters which control the deposition process, i.e. the stability constants of complex ions, differential double layer capacitance, crystal nucleation and growth, and the rate constants of the electron transfer process. Only limited information is available in this area.

There are certain disadvantages of electrolytic plating from molten salts. The main disadvantage is that, unless special precautions are taken, the metal coatings produced will lose their coherence. Other drawbacks include: possible annealing of the substrate at the process temperature which can lead to a reduction of hardness and to geometrical distortions; practical limitations can also arise from factors such as the corrosion of the plating cell and electrode materials.

5. Electrodeposited coatings from molten salts

A number of general reviews on the electrochemistry of molten salts are available. An extensive survey of the field up to about 1963 has been made by Reddy [71] and thereafter by Inman and co-workers [72–75] and others [55, 76]. All these reviews contain a useful section on electrocoating processes. Review articles specifically written on various aspects of electrodeposited coatings from molten salts are also available [1, 4, 6, 17, 21, 28, 77].

The work of Cook [1, 12, 13, 57] and Danzig (and co-workers) [78] involves metalliding a large variety of metals and alloy surfaces. Altogether twenty-five metals were found to be alloying agents (diffusing metals) and more than forty different metals were used as substrates. The typical metalliding elements include B, Si, Ta, Zr, Al, Cr, Sc, Ni, Ge, Y, and rare earths. Most of these studies were carried out to demonstrate the versatility of the technique and not much information is available in the open literature. Similar work was further extended by Withers *et al.* [14]. This work mainly includes berylliding, boriding, siliciding, aluminiding, titaniding, and chromiding a large variety of metal and alloy surfaces. Danzig *et al.* [78] tantalided nickel and AISI Type 316 stainless steel for applications requiring acid-resistant materials.

Stetson [79, 80] obtained titanium electrodeposits from molten fluorides up to 1000 μm thick on iron and other metal surfaces. These

coatings had high resistance to sea water, salt spray, and some chemicals. Inconel and AISI 321 substrates were found excellent for titanium coatings. Metals that interdiffuse slowly with titanium will make poor substrates. The plating rate varied between 50 and 1.25 $\mu\text{m h}^{-1}$ at a plate thickness of 750–875 μm .

Brookes *et al.* [81] studied the mechanism of boriding iron from molten salts. The coating produced had a hardness of ~ 2000 VPN. The effect of temperature on the rate of formation of boride layer in electrolytic boriding of iron bases from melts based on $\text{Na}_2\text{B}_4\text{O}_7$ and KBF_4 was investigated by Danek and Matiasovsky [82]. An equation to predict the time required for the formation of a boride layer of a definite thickness at a given temperature was proposed. Bowles and Newdick [83] studied the chromizing of mild steel from molten fluorides. The coating produced had excellent corrosion-resistant properties but had a disappointingly poor surface finish. The surface hardness was ~ 105 VPN. The comparatively high value of hardness obtained was caused by the excess of chromium present in the surface layer. Electrochemical boriding of molybdenum from molten fluorides was studied by Bonomi *et al.* [84]. A compact layer of Mo_2B_5 was formed on the surface of the metal. The discharge of boron on the cathode occurred with $\sim 100\%$ Faradaic efficiency.

Fellner and Matiasovsky [85] reported on diffusion coatings of silicide on stainless steels and Nimonic-type alloys, obtained from cryolitic melts of the type $\text{Na}_3\text{AlF}_6\text{-SiO}_2\text{-Al}_2\text{O}_3$, by chemical and electrolytic methods. With the latter method it was found that, at a temperature of 1020°C and cathodic current densities of 500–2000 A m^{-2} , a bright homogeneous silicide layer with an average composition corresponding to M_3Si was formed at the cathode. The coating had good hot corrosion properties (especially with respect to vanadium corrosion). The influence of current density and duration of electrolysis on the thickness and quality of the silicide layer was also studied. For an electrolysis time of 10 min and at current densities varying between 500 and 2500 A m^{-2} , the maximum thickness of coatings obtained on stainless steel and Nimonic alloy was 140 and 95 μm respectively. Excellent quality diffused silicide coatings on molybdenum have been

obtained from molten fluorides by Petrescu *et al.* [86] for protection against high temperature oxidation. The layer thickness was in the range 15–70 μm for the runs performed at 700°C for 2 h, the thickness being in general proportional to the current density for the range 100–300 A m^{-2} . The relatively low temperature, i.e. below the recrystallization point of molybdenum employed in this process, has the advantage of not impairing the creep resistance of the base metal.

Earlier work on electrolytic diffusion coatings has been reviewed by Reddy [71] and Senderoff [17]. A process [10] which describes the deposition of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, or W from molten fluoride melts is worth mentioning. A large number of substrates, i.e. nickel, iron, steel, copper, brass, bronze, etc., were electrocoated. It was found that hard intermetallic compounds could be formed on the surface by the diffusion of carbon, nitrogen, boron, or silicon into the surface layer. Hardness values \sim 400–1000 Vickers and coating thicknesses from many microns to a fraction of a micron were reported.

The deposition of protective coatings by electroplating from molten salts has been mainly confined to refractory metals. Some of the electroplated coatings are partially converted to diffusion coatings during the deposition process, because of the high temperatures employed, whereas others are given a post-heat treatment to diffuse the deposit into the base metal [8, 9, 11, 87–89].

Mellors and Senderoff [5, 16, 17, 27, 50, 63, 68–70, 90–96] electrodeposited coherent coatings of most of the refractory metals, i.e. Zr, Hf, V, Nb, Ta, Mo, W, Cr, some of their alloys, and zirconium diboride, using alkali fluoride refractory metal melts. Titanium could not be deposited coherently using this process. The successful work reported was concerned with single metal plating, a co-deposited compound coating [91], i.e. ZrB_2 , as well as co-deposited alloy coating [63], i.e. Zr–Ti, Zr–Al. It was not only possible to produce solid sheets of refractory metals for direct mechanical processing [16] but also to produce electroformed objects of complex shape [27]. This process has been reported [6] to be used successfully on a production scale for the electrodeposition of four of the metals: Nb, Ta, Mo, and W. Senderoff and Brenner [97] also studied plating of molybdenum from molten chlorides.

Recent progress made in the understanding of the fundamental mechanisms of the processes used to electrodeposit refractory metals from molten salts have been critically reviewed and comprehensively studied by Inman and co-workers [18, 21, 28, 40–42, 67, 98] and others [5, 16, 17, 66]. In a more recent publication [22] Inman has also outlined the underlying principles governing the formulation of molten salt baths for the electrodeposition of these metals. Optimum design factors and limitations involved in producing a practical electrolytic cell for the production of refractory metals by electrolysis of molten salts are also reviewed [21, 99].

Tokumoto *et al.* [100, 101] described a process for the electrodeposition of titanium from chloride melts in the temperature range 400–500°C. Flat and smooth electrodeposits of titanium on stainless steel with coating thickness up to \sim 0.5 mm were reported. The purity and microhardness were claimed to be comparable with the deposits obtained by the Kroll process [15].

Balke [102] and Eckstein and Ashton [103] also studied the deposition of tantalum and niobium from molten fluorides. Metal deposits produced [103] had a density of at least 98% of the theoretical density of the metal deposited, and the coatings were generally mechanically deformable without breaking and substantially free of non-metallic impurities. The process was capable of producing metal foils. The substrates which may be plated satisfactorily by this process include Ni, Cu, Mo, steels, graphite, etc.

One of the unique examples of electrodepositing a refractory metal from oxide melts was reported by Davis and Gentry [104]. They deposited a tungsten coating on a nickel substrate from a melt consisting of $\text{NaLiB}_2\text{O}_4 + \text{NaLiWO}_4 + \text{WO}_3$ (6:2:1 parts) at 900°C. The hardness of the deposits was \sim 425 H_v comparable with that of commercial tungsten. The coating thickness of up to 20 mils* was produced with 85–100% current efficiency of the process. Balikhin and Pavlovskii [105] also electrodeposited tungsten on nickel and molybdenum substrates from a melt having the composition $\text{NaCl} + \text{NaF} + \text{WO}_3$ (6:15:25 wt%) at 900°C. The tungsten coating had a microhardness value of \sim 450–500 kg mm^{-2} . The coating thickness up to 20 μm was easily produced. Tungsten coatings produced by this * 0.001 in.

method have an application as a barrier layer in composite and laminated materials.

Recently a molten salt electrolytic process ('Degussa') for the deposition of highly adherent and ductile coatings of platinum has been developed [7, 29, 30]. The process is suitable for plating Ti, Ta, Nb, Mo, W, Cu, Ni, steels, graphite, and ceramics, such as alumina. The mechanical properties of the deposit, generally 2–20 μm thick, are indicated and applications in electroplating, e.g. titanium anodes for chromium baths, electrochemical processes, corrosion protection, brazing, and wire products are outlined.

A method for the electrodeposition of TiB_2 from an oxide melt at 900°C has been developed by Schlain *et al.* [106, 107]. A current density of 6 A dm^{-2} produced a plating rate of $\sim 35 \text{ mm h}^{-1}$. The adherence of the TiB_2 deposit varied with the substrate material. Adherence was very good with Mo and 4130 steel, if these were given a pre-coat with Cu and Ni. Frazer *et al.* [87] studied the electrodeposition of ZrB_2 on Ni from oxides (B_2O_3 , ZrO_2) dissolved in molten cryolite. The ZrB_2 deposit was mainly scaly and/or dendritic and was usually non-adherent.

A new LDC-2 coating (Pt + Al) for nickel alloys has been obtained by electrolytic deposition followed by heat treatment [88]. The coating imparts improved hot corrosion and high temperature oxidation resistance. In another study [108] electroplated coatings of Ti, Zr, Mo, Cr, or V obtained from molten chloride baths were also converted to diffused coatings by a post-heat treatment. A coating of nickel on copper obtained from molten chlorides at 700°C was reported [109] to have been converted to diffusion coating during the duration of electrodeposition process.

Electrolytic metal plating from fused salts, with special reference to Sn plating of Fe and Cu bases, Zn plating of Fe bases, and Ti plating of Fe bases, have been reviewed by Matiasovsky *et al.* [4, 89]. More recently, electrolytic plating with aluminium or alloys of aluminium from low melting molten chlorides are attracting attention as an alternative to cadmium plating [23–26].

6. Properties of the electrodeposited coatings from molten salts and their applications

There is not a great deal of published information

on the mechanical properties of the electro-deposited coatings from molten salts. The quality of the metallized coatings obtained has already been discussed. Numerous examples of diffused surface coatings obtained on a variety of substrates have been reported by Cook [1, 13, 57]. Some of the typical properties of the metallized iron and various steel surfaces, which mainly result in improved corrosion resistance and hardness, are briefly summarized in Table 2.

Typical properties of the electroplated (non-diffused) refractory coatings obtained on various substrates such as steel, stainless steel, graphite, copper, Hastelloy alloys, and others, have been reported by Mellors and Senderoff [5, 17]. The deposits are usually dense and coherent with purity greater than 99.98%. The appearance and smoothness of the plates have been claimed to be comparable with deposits obtained from a Watts nickel solution at equivalent thickness. Deposits as thick as 6.4 mm have been produced with only slight roughness. The microstructure is usually columnar with the grain size increasing with thickness, as with typical electrodeposits from aqueous systems without addition agents.

Some of the main features of the coatings, both diffusion and plated, obtained by various workers have been described in the preceding section. Some additional information is summarized in Table 3.

Metallic coatings offer economy and technological advantages. Where resistance to oxidation or corrosion is the main consideration, a thin layer of alloying elements at the surface of a part is generally considerably less expensive than a solid alloy body. The bulk of an object may be of a cheaper or mechanically more suitable material, e.g. some form of iron.

There are many technological applications where materials are required to withstand high temperatures and very corrosive environments. These properties may be achieved by the application of a protective coating to a base metal or alloy, e.g. aluminide coatings on superalloys for aeroengines.

Surface coatings may be used to develop special wear-resistant or non-frictional properties, to produce a surface having definite electrical or magnetic properties, or to improve wetting characteristics and welding properties.

Table 2. Metallized iron and various steel surfaces with improved corrosion resistance and hardness. All the alloys mentioned in this Table contain more than 50% iron

<i>S No.</i>	<i>Metallizing metal</i>	<i>Metallized metal compositions</i>	<i>Description of coating</i>	<i>Reference</i>
1	boron	Iron, SAE 4140 steel, AISI 410 steel AISI 304 steel, A286 SAE 2320 steel and SAE 3151 steel	extremely hard, Knoop hardness numbers, KHN \approx 1500–2500 or > 3000 improved hardness and frictional properties	[1, 13, 57]
2	titanium	mild steel, Rodar, 304 stainless steel	smooth, shiny, very hard moderately flexible and resistant to concentrated nitric acid	[1, 13]
3	tantalum	1020 mild steel, 4340 tool steel	increased corrosion resistance	[1, 13]
4	aluminium	CR steel (1015) 304 stainless steel Fe (82%), Cr (18%) Kovar 4140 steel	smooth, hard, flexible, resistant to nitric acid and oxidation at high temperature smooth, shiny, hard, very flexible, improved resistance to nitric acid smooth, shiny, hard, and flexible smooth, shiny, very hard, flexible smooth, shiny, moderately hard, and flexible	[13, 57]
5	chromium	iron, CR steel, low carbon steel, AISI 403 steel	improved corrosion resistance	[13]
6	manganese	Ti-Namel, Rodar, 304 stainless steel	bright, smooth, soft, and flexible coating	[13]
7	vanadium	1015 CR steel, Fe–Cr (28% Cr), borided Ti-Namel, 304 stainless steel	smooth and very hard coatings	[13, 57]
8	zirconium	mild steel, Rodar stainless steel	hard, very resistant to nitric acid moderately hard, very resistant to nitric acid	[57]

7. Conclusions

Although considerable success has been reported in molten salt electrocoating processes, the theoretical understanding has not yet been developed to the stage where it is possible to design plating baths entirely from basic principles. A higher level of technical know-how must be required by new workers in this field than is required for aqueous electroplating baths. This has been pointed out by Wurm [7] as one of the

possible reasons why only five industries apply molten salt electrocoating commercially (excluding metallizing).

Some progress in our understanding of the mechanism of the electrodeposition processes from molten salts has been made. Many questions relating principally to the mechanism of deposition, the influence of small quantities of complex ion additives, and an assessment of the way they affect the rates of deposition processes, still require further investigation.

Table 3. Preparation and properties of the electrodeposited coatings from molten salts

S No.	Deposited metal(s)	Melt	Temperature (°C)	Substrate	Deposition characteristic	Major characteristics	Reference
1	Mo	CaCl ₂ -CaMoO ₄ + 5 wt% CaO ⁺	900-1000	Cu, Ni, Fe, steel, graphite	$i_c = 5-20 \text{ A dm}^{-2}$ anode = Mo under air	metal yield = $0.36-0.42 \text{ g A}^{-1} \text{ h}^{-1}$ speed of deposition = $0.29-1.37 \text{ } \mu\text{m min}^{-1}$ coating thickness = 1 mm microhardness = $190-230 \text{ kg mm}^{-2}$	cited in [20]
2	Mo	NaCl-KCl + 10 wt% MoCl ₃	600-900	stainless steel	$i_c = 3-30 \text{ A dm}^{-2}$ $i_a \leq 1 \text{ A dm}^{-2}$ anode = Mo under argon	metal yield = $1.193 \text{ g A}^{-1} \text{ h}^{-1}$ speed of deposition = $0.6-5.97 \text{ } \mu\text{m min}^{-1}$ coating thickness = 0-0.5 mm	[17, 97]
3	Mo + (1-10) wt% Ni	NaCl-KCl + 10 wt% MoCl ₃ + 5 wt% max. Ni	600	stainless steel	$i_c = 3 \text{ A dm}^{-2}$ $i_a \leq 1 \text{ A dm}^{-2}$ anode = Mo under argon	-	[17]
4	Zr	LiCl-KCl + 5 wt% K ₂ ZrF ₆	550	steel 108 KP	$i_c = 0.5-1 \text{ A dm}^{-2}$ $i_a = 0.2 \text{ A dm}^{-2}$ anode = Zr under argon	metal yield = $0.818-0.824 \text{ g A}^{-1} \text{ h}^{-1}$ speed of deposition = $1.05-2.07 \text{ } \mu\text{m min}^{-1}$ coating thickness = 0.1-0.2 mm	cited in [20]
5	Zr	LiF-KF-NaF + 16.9 wt% K ₂ ZrF ₆	750	Mo	$i_c = 5-10 \text{ A dm}^{-2}$ $i_a = 1 \text{ A dm}^{-2}$ anode = Zr under argon	metal yield is up to $0.85 \text{ g A}^{-1} \text{ h}^{-1}$ speed of deposition = $0.22-0.66 \text{ } \mu\text{m min}^{-1}$ coating thickness = 0-2.5 mm	[17, 63]
6	ZrB ₂	LiF-KF-NaF + 12 wt% KBF ₄ + 16.9 wt% K ₂ ZrF ₆	800	Mo	$i_c = 3 \text{ A dm}^{-2}$ anode = Zr under argon	coating thickness = 0-0.3 mm	[17, 63]

Table 3. (continued)

S No.	Deposited metal(s)	Melt	Temperature (° C)	Substrate	Deposition characteristic	Major characteristics	Reference
7	Zr-Al	LiF-KF-NaF + 16.9 wt% K ₂ ZrF ₆ + 1 wt% Al ₂ O ₃	750-800	Mo	$i_c = 3 \text{ A dm}^{-2}$ anode = Zr under argon	-	[17, 63]
8	Zr-Ti	LiF-KF-NaF + 15 wt% K ₂ ZrF ₆ + 16.9 wt% K ₂ TiF ₆	750-800	Mo	$i_c = 3 \text{ A dm}^{-2}$ anode = Zr under argon	-	[17, 63]
9	Hf	NaCl-KCl + (4-15) wt% HfCl ₄	750-800	Mo	$i_c = 25-50 \text{ A dm}^{-2}$ $i_a = 1 \text{ A dm}^{-2}$ anode = Hf under argon	metal yield = $1.66 \text{ g A}^{-1} \text{ h}^{-1}$ speed of deposition = $5-10 \mu\text{m min}^{-1}$ coating thickness = 0.05 mm microhardness = 400 kg mm^{-2}	cited in [20]
10	V	LiCl-KCl + 5 wt% VCl ₂	400	Mo, Ti, Ni, Fe, steel	$i_c = 1-2 \text{ A dm}^{-2}$ $i_a = 1 \text{ A dm}^{-2}$ anode = V under argon	metal yield = $7-6 \text{ g A}^{-1} \text{ h}^{-1}$ speed of deposition = $0.2-0.6 \mu\text{m min}^{-1}$ coating thickness = $3-5 \text{ mm}$ microhardness = $60-70 \text{ kg mm}^{-2}$	cited in [20]

Coatings to protect structural materials, e.g. superalloys, against oxidation and sulphidation at elevated temperatures have become important only in recent years. Diffusion coating from molten salts offers a promising technique for protection against oxidation, corrosion, and wear. Further development work in this area to extend this technique to multi-element coatings could be technologically rewarding.

Aluminium or aluminium alloy electroplating from low melting melts offer a promising alternative to aqueous cadmium plating for many applications.

Acknowledgements

The author is grateful to Mr J. M. Herbert and Mr N. F. Jackson for their helpful criticism of the manuscript and suggestions; to Dr D. Inman (Imperial College of Science and Technology, London), and to Dr G. W. Mellors (Union Carbide, USA) for providing lists of their publications and reprints/preprints on electrodeposition. He is also grateful to the Ministry of Defence (PE) for financial support for a part of the work and to the Plessey Company Limited for permission to publish this Paper.

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