# Electrolytic metal coating in molten salts

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Electrolytic coating of metals appears to be a promising field of exploitation of molten salts and is gaining a steadily increasing interest in the surface technology, namely in the anticorrosive protection and surface hardening of various metallic substrates. The main advantages of the electrolytic metal coating in molten salts in comparison with the conventional methods are simultaneously the high rate and the possibility of an exact regulation of the coating process.

Based on the characteristic features of the electrodeposition, the reviewed processes were divided into four groups:

(i) Coating by low-melting heavy metals
(ii) Aluminium-plating
(iii) Coating by refractory metals
(iv) Formation of diffusion coatings

For each group, the problems involved are demonstrated in detail for one typical metal or element whilst the plating processes by other metals of the respective group only are concisely surveyed.

Электролитическое покрытие металлов является многообещающей областью использования расплавов солей и пользуется постоянно растущим интересом исследователей в области поверхностной технологии, а именно, для антикоррозионного покрытия и поверхностного отверждения различных металлических субстратов. Главным преимуществом электролитического покрытия металлов в среде расплавов солей по сравнению с обычными методами является его большая скорость и одновременно возможность точного управления процессом покрытия.

Исходя из характерных черт электроосаждения, рассматриваемые процессы были разделены на четыре группы:

(i) Покрытие низкоплавкими тяжелыми металлами
(ii) Покрытие слоем алюминия
(iii) Покрытие тугоплавкими металлами
(iv) Создание диффузных покрытий

Для каждой группы демонстрируются свойственные ей проблемы на примере одного типичного металла или элемента, в то время, как процессы покрытия другими металлами соответствующей группы обозреваются вкратце.

The molten salts, which represent the most concentrated ionic liquids, appear to be a highly interesting object of investigation both from the aspect of the scientific research as well as with respect to their present or potential technological exploitation. Beside the traditional utilization in the extraction of metals (aluminium, magnesium, sodium, *etc.*), the research of molten salts created a basis for the development of new promising fields of their exploitation, *e.g.* in the processing of metals and elements, in the treatment of metals, in the energy production and storage (advanced batteries, fuel cells, thermal energy storage, nuclear and solar energy production), in the industrial organic and fuel chemistry, as leaching or solvent extraction agent, *etc.* An excellent comprehensive review covering most domains of the present or potential technological interest in molten salts has been published quite recently [1]. It should be pointed out, however, that the electrocoating of metals from molten salts which appears to be one of the promising fields of their potential exploitation only is marginally dealt with by *Kerridge* and *Lovering* [2] (except for diffusion coating — see later) and by *Lovering* and *Williams* [3] in the above review. For information on metal plating, the reader is merely referred to a 1972 paper by *Matiašovský et al.* [4] and to reviews by *Galopin* and *Daniel* [5] and by *Sethi* [6].

The formation of a protective layer of metal which is resistant to the chemical and/or electrochemical activities of the medium concerned appears to be one of the most effective methods of the anticorrosive protection of metals. Beside the conventional methods of metal-plating, *e.g.* hot plating in molten metals or the electroplating in aqueous solutions (galvanizing), in the last two decades the possibility of electrolytic metal-plating in molten salts has been systematically studied, both with "traditional" materials (tin or zinc), and with other metals, such as aluminium and the rare metals, namely refractory metals (beryllium, titanium, zirconium, *etc.*). The investigation of the surface treatment of metallic substrates in molten salts also includes the diffusion coating, *i.e.* the saturation of the surface of the base by elements, such as boron, carbon, silicon or nitrogen, under formation of "intermetallic" compounds or diffusion layers with outstanding mechanical and/or anticorrosive properties.

The fundamental conditions for a good binding between the base metal and the protective layer are the same as in other plating methods, *i.e.* the formation of solid solution and/or of intermetallic compounds in the underlayer at the boundary of the two metals.

As shown elsewhere [4, 7], the electrolytic metal-plating in fused salts exhibits some obvious advantages compared to electroplating in aqueous solutions, mainly a higher current density (generally by an order of magnitude) and, consequently, a higher productivity of the plating process, a better binding between the deposited metal and the substrate, and a better quality, namely the anticorrosive resistance of the coatings. Besides, in molten salts also coatings

528

can be prepared of metals which cannot be deposited electrolytically in aqueous solutions owing to their position in the electrochemical potential series, *e.g.* aluminium. In comparison with the hot plating processes, the main advantages should be the possibility of an exact regulation and the economy of the plating process. In some cases (*e.g.* in aluminium-plating) also a lower operating temperature compared to that used in the corresponding hot plating process may be of a definite importance.

In numerous papers on electroplating in molten salts which have been reviewed by *Galopin* and *Daniel* [5] and *Sethi* [6], the authors adopted an empirical approach to the investigated problem. In most cases, however, the rationalization of the plating processes depends on the solution of some fundamental problems of both theoretical and technical character, mainly concerning the composition, physicochemical properties and ionic constitution of the electrolyte, composition and structure of the underlayer and structure of the deposited metallic layer, problems related to the mechanism of the electrode processes, electrocrystallization of the deposited metal (for metals with the melting point above the operating temperature), the optimum processing parameters in the electrolysis, *etc.* As will be shown later, these data are far from being complete and extensive research must be carried out in this field in order to fill up the existing gaps.

When considering the characteristic features of the electrodeposition and formation of coatings of the respective metals, the reviewed processes can be divided into four groups:

  (i) Coating by low-melting heavy metals at temperatures above their melting point
  (ii) Aluminium-plating at a temperature below its melting point
  (iii) Coating by refractory metals
  (iv) Formation of diffusion coatings (electrolytic cementation)*

With regard to the limited extent of this review, for each group the problems involved will be demonstrated in detail for one "typical" metal or element whilst the plating processes by other metals of the respective group will only be concisely surveyed.

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* Metal-plating (groups (i)—(iii) processes) produces continuous and coherent metal coatings of the deposited metal on the substrate, whereas in the group (iv) processes the deposited elements diffuse fully into the substrate under formation of diffusion coatings (surface alloys) consisting of intermetallic (or pseudo-intermetallic) compounds and/or solid solutions. The latter processes have also been referred to as metalliding. This denomination, however, is not quite correct as the diffusion coatings can be formed also by the diffusion of a non-metallic element (*e.g.* boron).

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## Electroplating by the low-melting metals

The group of the low-melting metals deposited at temperatures close to their melting point (m.p.), which may be of interest with respect to electroplating, includes (in order of increasing m.p. given in parenthesis): indium (156.6°C), tin (231.9°C), bismuth (271.3°C), thallium (303.5°C), cadmium (320.9°C), lead (327.5°C), zinc (419.5°C), and antimony (630.7°C).

Most attention has been paid to tin-plating of iron (steel) and copper substrates which reached the pilot scale. The investigation into the possibility of deposition of coherent Zn, Pb, Cd, Bi, In, and Tl coatings (in order of the frequency of the relevant papers and patents) did not reach over the laboratory scale studies, and no information was found on antimony-plating. The electrodeposition of Sb as well as of Bi and Pb was investigated mainly with respect to their refining in molten salts [8].

The problems encountered in the investigation will be demonstrated for tin where the electroplating process is rather well understood.

### Tin-plating

The conventional processes used in tin-plating, *i.e.* the hot plating and the electrolytic method of Sn-plating in aqueous solutions, have some serious drawbacks. The main disadvantage of the hot plating process appears to be a high consumption and a relatively low coefficient of utilization of Sn (0.80—0.85). Compared with this method, electroplating in aqueous solutions has some advantages such as a lower Sn consumption and a higher coefficient of utilization, the possibility of an exact regulation of the thickness of the Sn coatings, *etc.* However, the efficiency of this procedure is fairly low and the deposited Sn-layer has to be thermally treated with regard to the great porosity and the low rate of the underlayer formation. It may be assumed that electrolytic tinning in fused salts could combine the advantages of both the above methods, especially with regard to the efficiency of the electrolytic process and the quality of the deposited layers. Concerning the anticorrosion resistivity of the protective layer, the porosity appears to be one of the most important criteria. From the data reported by *Plotnikova* and *Andreeva* [9] it follows that the quality of the Sn layer deposited in molten salts is clearly superior to that obtained by conventional methods of tinning.

Probably the first paper on Sn-plating in molten salts was published by *Alabyshev* and *Zhukova* [10]. Later, this problem was investigated by *Vitkin* and coworkers [11, 12] (numerous papers published mostly by Soviet authors up to 1964 have been reviewed by *Delimarskii et al.* [13]) and by several other authors [9, 14—17].

The system $SnCl_2$—KCl has been generally used as the fundamental electrolyte, in some cases with an addition of $ZnCl_2$*. The recommended "optimum" composition of the fundamental electrolyte varies from that corresponding to the compound $SnCl_2 . KCl$ (71.8 mass % $SnCl_2$ + 28.2 mass % KCl, m.p. = 225°C [18]) through the melt consisting of 80 mass % $SnCl_2$ and 20 mass % KCl (corresponding essentially to the eutectic composition in the subsystem $3SnCl_2 . KCl$—$SnCl_2 . KCl$ in the system $SnCl_2$—KCl with the eutectic temperature of 176°C [18]) to the composition of $3SnCl_2 . KCl$ (88.4 mass % $SnCl_2$ + 11.6 mass % KCl, m.p. = 218°C [18]). $ZnCl_2$ (5 to 12 mass %) is either added to the fundamental electrolyte or substituted (partly) for KCl, mainly in order to improve the surface properties of the electrolyte [19]. The electrolysis has been carried out at temperatures from 240 to 400°C (preferably at 300 to 320°C) with cathodic current densities up to 10 A cm$^{-2}$ (substantially higher current densities have been used by *Schnable* and *Javes* [15] in special application — see foot-note).

The literature data on the optimum electrolyte composition and processing parameters (cathodic current density, temperature) in Sn-plating of an iron base have been systematically reexamined by *Matiašovský* and coworkers [4, 7, 20] at temperatures both below and above the m.p. of Sn. Besides, the same parameters were determined for a Cu base.

The electrodeposition of tin below its melting point was carried out at temperatures 200, 210, and 220°C and cathodic current densities ($j_c$) from 0.5 to 2.5 A cm$^{-2}$. Three different electrolytes were tested: (i) eutectic mixture $SnCl_2$—KCl (80 mass % $SnCl_2$ + 20 mass % KCl), eutectic temperature 176°C, (ii) mixture of 70 mass % $SnCl_2$ and 30 mass % $ZnCl_2$ with the temperature of the primary crystallization ($\theta_{pc}$) 180°C, (iii) eutectic mixture $SnCl_2$—KCl with an addition of 5 mass % $ZnCl_2$. At low temperatures and current densities, tin was deposited in the form of dendrites or powder. Coherent Sn coatings were only obtained at temperatures higher than 220°C and current density above 2.5 A cm$^{-2}$ when liquid coatings were formed due to overheating of the iron base (cathode). In the initial stage of the electrolysis, the crystallization nuclei of tin on the surface of the base developed into droplets. With additional Sn deposited, the droplets fused to form a coherent liquid coating. The size, number, and uniformity of distribution of the Sn droplets were found to depend mainly on the composition of the electrolyte, the ternary $SnCl_2$—KCl—$ZnCl_2$ mixture being clearly superior in this respect to the binary electrolytes (i) and (ii). It is

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* *Schnable* and *Javes* [15] have used pure $SnCl_2$ or a 70 mass % $SnCl_2$ + 30 mass % $ZnCl_2$ mixture. Their study, however, was oriented rather on the deposition of tin and other low-melting metals or alloys on the ends of wires, strips or rods to use the deposits as solders or as alloying systems in fabrication of electronic devices such as transistors.

assumed that the formation of Sn coatings deposited at temperatures above the m. p. of tin can be described by the same mechanism.

In the investigation into the tin-plating of Fe and Cu bases at temperatures above the m. p. of tin, the binary $SnCl_2$—NaCl, $SnCl_2$—KCl, $SnCl_2$—$ZnCl_2$ and the ternary $SnCl_2$—NaCl—LiCl, $SnCl_2$—NaCl—KCl, $SnCl_2$—NaCl—$ZnCl_2$, and $SnCl_2$—KCl—$ZnCl_2$ mixtures were tested as electrolytes. The electrolysis has been carried out at temperatures 250, 300, 350, and 400 °C with current densities varying from 1 to 13 A cm$^{-2}$ in both an inert (argon) and an open atmosphere.

The appearance and structure of a deposited Sn-layer on both Fe and Cu bases are determined by a series of different factors, namely by the composition of the electrolyte, the temperature and duration of the electrolysis, the regime of cooling, *etc.* The surface of Sn layers which were deposited in binary molten mixtures was not smooth both on the Fe and Cu base though the macro-look was better in the first case. Under the microscope, a multitude of small droplets was visible. An increase in the working temperature somewhat improved the appearance of the layer. In the electrolysis of the ternary mixtures an expressed beneficial effect of the $ZnCl_2$ addition to the basic binary $SnCl_2$—NaCl and $SnCl_2$—KCl mixtures on the uniformity and the micro- and macroscopic appearance of the Sn layers, most probably due to the influence effected by $ZnCl_2$ on the interfacial tension at the electrolyte/cathode boundary, was determined [4]. The deposited Sn layers were continuous, uniform, and non-porous, of a polycrystalline texture. They consisted of $\beta$-Sn grains of almost uniform size, the individual grains being formed by the oriented crystallites.

The cathodic current density within the range 1—13 A cm$^{-2}$ did not effect any significant influence on the quality of the deposited Sn coatings. At $j_c >$ $> 13$ A cm$^{-2}$ the unfavourable effect of the concentration polarization (deposition of non-uniform coatings) has been observed in stationary electrolysis.

On the basis of experimental results, *Lubyová* and *Matiašovský* [21] recommended the following "optimum" composition of the electrolyte: 76—84 mass % $SnCl_2$, 8—12 mass % alkali chloride (preferably KCl), and 8—12 mass % $ZnCl_2$.

The operating temperature should be about 300 °C.

When considering the "optimum" current density of the tinning process, it should be taken into account that the tin coating is carried out essentially in two steps:

(i) formation of the underlayer,
(ii) formation of the tin layer.

The second step only is determined by the value of the cathodic current density whilst the first step is governed by the diffusion of Sn into the base and its

reaction with the substrate which depends mainly on time and temperature.*

According to the respective positions of Fe and Sn in the electrochemical potential series, iron reacts with the $SnCl_2$-based electrolyte under formation of the metallic Sn by the exchange reaction

$$Fe + Sn^{2+} \quad \rightleftarrows \quad Sn + Fe^{2+} \qquad (A)$$
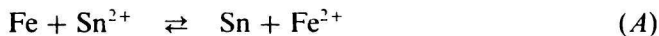
which takes place also during electrolysis, its rate relatively decreasing with increasing cathodic current density. According to the data on the system $Sn|SnCl_2$ (or $SnCl_2—KCl$)|Fe, it represents a short-circuited galvanic element with an iron cathode on which tin is deposited [23].

The composition of the underlayer at the boundary between the base metal and the deposited Sn-layer was determined by means of X-ray phase analysis and the electron microprobe. It was found [4] that the underlayer on an iron base is formed by a layer of a solid solution of Sn in Fe, a layer of intermetallic compound $FeSn_2$ and a thin layer of a solid solution of Fe in Sn. No separate phase corresponding to the intermetallic compound FeSn which was found in the phase equilibria study in the system Fe—Sn [24] was identified.

It may be assumed that the exchange reaction $(A)$ is favoured by the formation of $FeSn_2$. In the tinning of a Cu base, an analogous reaction can only occur most probably as a consequence of the formation of intermetallic compounds.

Three intermetallic compounds, $viz.$ $Cu_6Sn_5$, $Cu_3Sn$, and $Cu_{31}Sn_8$ were found in the system Cu—Sn [24, 25], the last one, however, only being stable at temperatures above 350 °C [24]. $Cu_6Sn_5$ and $Cu_3Sn$ have been identified in the underlayer on a Cu base [26].

As said above, the formation of the underlayer is governed by the diffusion of tin into the base metal which is accompanied by formation of intermetallic compounds. The diffusion processes on the Fe/Sn and Cu/Sn phase boundaries in the temperature range 200 to 450 °C were investigated by $Lubyová$ $et$ $al.$ [26]. The determined diffusion coefficients made it possible to determine the rate of formation of the underlayer at various temperatures, the calculated values being in good agreement with those determined experimentally by means of the method of galvanostatic anodic dissolution [27].

The reaction $(A)$ should be suppressed to a maximum degree in order to prevent the contamination of the electrolyte by $FeCl_2$. Even at low concentrations, $FeCl_2$ deteriorates the quality (homogeneity, appearance) of the Sn layer and the electrolyte becomes unoperable at a concentration of 1 to 2 mass %

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* It should be pointed out that according to the recent data reviewed by $Gálová$ [22], the corrosion resistance of the tin coatings in the anaerobic conditions is guaranteed by the $FeSn_2$ underlayer which makes the tin-plating in molten salts especially attractive.

FeCl$_2$ (at 350°C) [13]. The effect of reaction ($A$) decreases with increasing cathodic current density and essentially is entirely suppressed at $j_c \approx 6 \text{ A cm}^{-2}$ [20]. Consequently, this is the minimum current density at which the electrolysis should be carried out. At this current density, a tin layer with a thickness of 2 μm which guarantees a safe corrosion resistivity in most applications is formed in about 0.4 s. Based on the diffusion coefficients determined by *Lubyová et al.* [26], it was calculated that within this period underlayers with a thickness of 0.1 and 0.4 μm are formed (at 300°C) on iron and copper bases, respectively, which ensures a good binding between the base and the deposited Sn layer.

When operating at higher current densities (up to 13 A cm$^{-2}$), it has been suggested [4, 7, 20, 21] that the base should be exposed prior to electrolysis to the bath of the same composition as the electrolyte in order to obtain a suitable underlayer by the exchange reaction ($A$). This proceeding, however, seems to be unfavourable with respect to the economy of the tinning process as it would involve necessarily the purification of the bath.

The current efficiency was found to depend strongly on the current density. At low current densities, the current efficiency exceeds 100 % owing to the formation of metallic Sn by the exchange reaction ($A$). Besides, according to *Delimarskii et al.* [13], when using a soluble Sn anode tin can dissolve under formation of the subvalent Sn$^+$ cations which may result in a cathodic current efficiency exceeding 100 %. Here again, the effect depends on the current density. With cathodic current densities increasing from 0.5 to 2.5 A cm$^{-2}$, the average valency of Sn cations increased from 1.55 to 1.85.

It may be concluded that the current efficiency decreases with increasing cathodic current density and reaches 100 % at current densities between 5 to 6 A cm$^{-2}$ [28], this indicating that no side reactions are involved in the electrolytic process. At higher current densities, the current efficiency decreased to about 50 to 60 % at 13 A cm$^{-2}$. Thus it becomes obvious that the minimum cathodic current density value of 6 A cm$^{-2}$ is simultaneously the optimum current density.

With a soluble Sn anode and due to the lack of the cathodic and anodic overvoltage, the anodic dissolution and the cathodic deposition of Sn is an equilibrium process and the cell voltage as a driving force is mainly consumed to cover the ohmic voltage drop in the electrolyte. Owing to the high conductivity of the molten electrolyte (for the system 80 % SnCl$_2$ + 20 % KCl at 300°C, $\varkappa = 0.678 \text{ S cm}^{-1}$; for 3SnCl$_2$ . KCl at 300°C, $\varkappa = 0.935 \text{ S cm}^{-1}$ [29]), the operating voltage will depend on the experimental set-up, *i.e.* on the construction of the electrolytic cell.

The favourable effect of an inert atmosphere in the electrolysis, reported by *Chetverikov et al.* [30, 31] and by *Ivanova* and *Trifonov* [32] was not confirmed in stationary electrolysis which represents a closed system with gaseous phase

consisting of saturated vapours of the electrolyte, though *dry* atmosphere may be important in a continuous process.

Based on extensive research, *Delimarskii et al.* [13] designed a pilot-scale line for the continuous tinning of steel sheets. The electrolyte consisted of a mixture of 80 mass % $SnCl_2$ and 20 mass % KCl. The electrolysis has been carried out at a temperature of 300 to 320 °C with a cathodic current density within the range 3—10 A cm$^{-2}$. The cell voltage was from 8 to 10 V.

According to *Vitkin et al.* [33], it is advantageous to deposit a thin (0.01— 0.04 μm) nickel layer on the steel sheet prior to the proper Sn-plating. The Ni underlayer, which was deposited galvanically from aqueous electrolyte, suppressed the Fe contamination of the electrolyte and had a beneficial effect on the uniformity of Sn coatings which also exhibited an improved corrosion resistivity. Consequently, the thickness of the Sn coatings could be reduced to 0.5— 0.7 μm which makes the process acceptable from the economic aspect.

A process has also been developed for the continuous tinning of copper wires [28, 34, 35]. The melt containing 80 mass % $SnCl_2$ + 10 mass % KCl + 10 mass % $ZnCl_2$ (temperature of the primary crystallization 213 °C) has been used as the electrolyte. The electrolysis was carried out in the temperature range 240 —300 °C with a cathodic current density 0.4—10 A cm$^{-2}$, the optimum operating parameters being 300 °C and 6 A cm$^{-2}$. The tin coatings deposited under those conditions exhibited an outstanding corrosion resistivity, namely with respect to sulfur compounds, and good soldering properties.

### Zinc-plating

Based on the literature data, here also it can be assumed that the electrolytic Zn-plating in fused salts might combine the advantages of both the hot plating method and the galvanic zinc-plating in aqueous solutions.

*Bykova* and *Gorodyskii* [36] investigated into the possibility of the deposition of Zn on an iron base by the electrolysis of a melt containing 45.7 mass % $ZnCl_2$ + 54.3 mass % KCl* with an addition of 1 to 2 mass % $AlCl_3$. The anode consisted of liquid Zn. The electrolysis was carried out in the temperature range of 430—460 °C, the anodic current density being 0.5—1.5 A cm$^{-2}$, the cathodic current density 4—6 A cm$^{-2}$. Without $AlCl_3$ addition, no coherent Zn coatings could be obtained and in the binary $ZnCl_2$—KCl electrolyte zinc was always deposited in the form of powder and/or dendrites.

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* The composition of the basic electrolyte corresponds to the eutectic composition of the respective system. Due to the formation of two congruently melting compounds, there are three eutectic points in the system $ZnCl_2$—KCl [37].

The positive influence of an $AlCl_3$ addition has been confirmed by *Matiašovský* and *Lubyová* [4, 38, 39] in the Zn-plating of iron (low-carbon steel) substrates in $ZnCl_2$—NaCl—$AlCl_3$ and $ZnCl_2$—KCl—$AlCl_3$ mixtures. The following electrolyte compositions were found to be the most convenient:

System $ZnCl_2$—NaCl—$AlCl_3$: basic mixture containing 76.7 mass % $ZnCl_2$ + 23.3 mass % NaCl with an addition of 5 mass % $AlCl_3$.

System $ZnCl_2$—KCl—$AlCl_3$: basic mixture containing 68.4 mass % $ZnCl_2$ + 31.6 mass % KCl with an addition of 5 mass % $AlCl_3$. As optimum operating parameters, the temperature within the range 400—450 °C and cathodic current densities from 4 to 5 A cm$^{-2}$ were recommended. (Liquid Zn coatings were deposited even at 400 °C, *i.e.* below the m.p. of Zn (419.5 °C) due to the overheating of the cathode at high current densities.) Under those conditions, uniform and bright Zn coatings were obtained with a current efficiency of almost 100 %. The uniformity of the layers deposited in the $ZnCl_2$—NaCl—$AlCl_3$ electrolyte was found to be superior to those deposited in the electrolyte containing KCl.

The deposited Zn layers were of a polycrystalline texture. The underlayer consists mostly of intermetallic compounds with an average composition corresponding to $Zn_{10}Fe_3$ (major component), $Zn_7Fe$ and a thin layer of a solid solution of Zn in Fe.

The specific influence of $AlCl_3$ on the quality of the Zn coatings still remains unresolved. All attempts to substitute aluminium chloride by other Al compounds and various surface-active or desiccating substances have been unsuccessful [4, 39]. It should be mentioned, however, that an addition of aluminium into molten zinc bath for hot-dip coating exhibited a favourable influence on the kinetics of formation of intermetallic phases in the system Fe—Zn [40].

*Plating by other low-melting heavy metals*

The electrolytic deposition of the other low-melting metals in molten salts has been investigated rather with respect to electrowinning and/or refining than to deposition of the thin, coherent and corrosion resistant coatings, the only exceptions being cadmium and lead.

The possibility of cadmium-plating was investigated by *Delimarskii et al.* [41, 42] and by *Lindau* and *Sauerwald* [43]. Delimarskii and coworkers tested various mixtures based on cadmium chloride and claim the mixture consisting of 67 mass % $CdCl_2$ and 33 mass % NaCl to be the best suited as electrolyte. The electrolysis should be carried out at 450 °C and a cathodic current density of up to 1 A cm$^{-2}$ using an anode containing 90—92 mass % Cd and 8—10 mass % Al. The authors assume that aluminium decreases the interfacial ten-

sion on the Cd/substrate phase boundary which results in an improved wettability of the substrate by deposited cadmium (this may be considered as an analogy with the hot-dip Zn-plating process [40]). Under these conditions, coherent Cd coatings with a thickness from 4 to 20 μm were deposited depending on the operating parameters (time, current density). *Lindau* and *Sauerwald* [43] deposited Cd coatings from a bromide electrolyte consisting of 10 mass % $CdBr_2$ and 90 mass % $AlBr_3$ at 210 °C, *i.e.* below the melting temperature of cadmium. In this case, however, coherent coatings only were obtained at very low current densities (0.006—0.0075 A cm$^{-2}$) which makes this process rather unattractive with respect to a possible technological utilization.

The electrodeposition of lead coatings in chloride melts containing lead(II) chloride as the electrochemically active component was investigated by *Delimarskii et al.* [42, 44]. Coherent Pb coatings with a thickness of up to 150 μm were deposited in a mixture containing 5—8 mole % $PbCl_2$, 50—60 mole % $ZnCl_2$, and 32—35 mole % KCl with a Pb anode at 250—270 °C, *i.e.* below the melting point of Pb, however, with the cathodic current densities from 0.1 to 0.4 A cm$^{-2}$.

As to the possibility of deposition of indium, bismuth, thallium, and antimony coatings, a general information can be obtained from the literature data on the electrowinning of the corresponding metals. With respect to the bismuth-plating, the data on the bismuth deposition from the ternary $BiCl_3$—LiCl—KCl mixtures at 385—426 °C and 0.24—0.32 A cm$^{-2}$ [43, 45] seem to be of interest. Antimony was deposited from electrolytes based on antimony(III) sulfide. Promising results were achieved with multicomponent systems $Sb_2S_3$—$NaPO_3$—$KPO_3$—NaCl and $Sb_2S_3$—$Sb_2O_3$—$NaPO_3$—$KPO_3$—NaCl operating at 650 °C with a cathodic current density 0.9 A cm$^{-2}$ [46]. The electrodeposition of indium and thallium for special applications (see the foot-note in the paragraph on Sn-plating) has been investigated by *Schnable* and *Javes* [15]. Indium was deposited from pure indium monochloride, InCl, at 250 °C or from a mixture of 79 mass % InCl and 21 mass % $ZnCl_2$ at 265 °C using a soluble In anode. In the deposition of thallium, pure thallium monochloride, TlCl, was used as electrolyte, the operating temperature being 460 °C. In this case, an inert graphite anode has been used.

## Aluminium-plating

Aluminium-plating appears to be one of the most effective methods for surface protection of iron (steel) bases, mainly against reactions caused by humidity and sulfur compounds. At present aluminium-plating is done by the hot-plating process. The disadvantages are that the aluminium layer is excessively thick and coarse grained. The latter is caused by the formation of brittle

intermetallic compounds (most probably $Fe_2Al_5$ and $FeAl_3$) in the underlayer at the high temperature of the aluminium coating process [47]. Other less frequently used methods such as the diffusion process and the vacuum deposition have disadvantages from the economic point of view.

Electrolytic aluminium-plating is based on deposition from non-aqueous solutions, as the deposition potential of aluminium is much more negative than that of hydrogen. Essentially, there are two possible methods: electrolysis of aluminium compounds dissolved in organic aprotic solvents, and electrolysis in fused salts, mainly chlorides, where Al can be deposited either by the electrolytic decomposition of the electrochemically active component ($AlCl_3$), or by using a soluble aluminium anode. Various processes based on the former method have been recently reviewed by *Gálová* [22, 48].

Electrolysis in fused salts has several advantages compared to both hot-dip method and electrodeposition from organic solvents. The low temperature of electrolysis (below 200 °C) compared with the hot-plating process (about 700 °C) suppresses the formation of brittle intermetallic compounds in the underlayer [47]. The main disadvantages of the electrolysis of organic solutions compared to fused salts are a lower electrical conductivity (generally by one order), higher toxicity and inflammability of the solvent. This makes the Al-plating in fused salts potentially attractive for technological application.

Thus it is not surprising that the problems related to the electrolytic deposition of aluminium in molten chlorides have been investigated thoroughly in recent years. Besides the papers and patents reviewed by *Paučírová* and *Matiašovský* [49], a number of papers [50—62] and patents [63—70] dealing with various aspects of this method have recently been published. Most attention has been paid to the effect of the composition of the electrolyte and of the operational parameters of the electrolysis on the properties of the aluminium deposits.

Binary $AlCl_3$—$NaCl$ and ternary $AlCl_3$—$NaCl$—$KCl$ mixtures containing 75—82 mass % $AlCl_3$ (preferably close to the upper limit of this concentration range) have been used as electrolytes. In some cases other alkali or alkaline earth halides were added to the base electrolyte. In Al-plating of iron (steel) bases the electrolysis was carried out in the temperature range 160—200 °C at cathodic current densities of 20—50 $mA\,cm^{-2}$ depending on the composition of the electrolyte. It was found that after reaching a certain limiting value, denoted as the dendrite growth threshold current density [54] (in sake of simplicity denoted further as critical current density, $j_{cr}$), aluminium is deposited in the form of dendrites or powder. The same phenomenon was observed when a certain thickness of the aluminium layer has been deposited, and it was found that this critical thickness depends on the operational parameters of the electrolysis, *i.e.* on the cathodic current density and the time. A decrease in the concentration

538

of $AlCl_3$ in the ternary electrolyte below 75 mass % brings about a drastic decrease in the value of $j_{cr}$ (to below 1 mA cm$^{-2}$) [71, 72].

The common inadequacies of most of the proposed aluminium-plating methods in molten salts appear to be the low current densities (and consequently the low plating rate) and the high concentration of highly hygroscopic and volatile $AlCl_3$ in the electrolyte [49]. Thus it was obvious that the research in this field was to be oriented towards the solution of these fundamental problems, *i.e.* the possibility of increasing the value of the $j_{cr}$ and decreasing the concentration of aluminium chloride in the electrolyte, preferably to about 50 mole % $AlCl_3$ (69.5 mass % in the $AlCl_3$—NaCl system and 67 mass % in the $AlCl_3$—NaCl —KCl system) when all the $AlCl_3$ would be bound in the form of a relatively stable compound $MAlCl_4$ where M is sodium or potassium.

### Effect of additives

The low value of the $j_{cr}$ and the existence of a critical thickness of the aluminium deposits indicated the predominant role of the electrocrystallization of aluminium in the deposition process. Numerous attempts have been made to influence the process of electrocrystallization by codeposition of different metals which were added to the electrolyte in the form of compounds (chlorides or oxides), or as auxiliary anodes of the respective metals. Some of them, namely Sn, Pb [67, 74—78], and Mn [79], improved the appearance and corrosion resistivity of the deposited layers (in all cases the corresponding alloys were deposited), which was important especially in the aluminium-plating from the binary $AlCl_3$—NaCl mixtures where Al was deposited in the form of dull, coarse-grained coatings with a low corrosion resistance. The codeposition of these metals, however, did not offer the possibility to solve the main problems mentioned above.

More promising results were achieved with application of surface-active substances (surfactants) to the base electrolyte. The moderate operating temperature makes it possible to use also organic surfactants which were found to be highly effective in galvanic metal-plating processes in aqueous solutions. *Delimarskii* and coworkers [64, 66, 73] have tested a series of surfactants and claimed urea and $\alpha$-naphthylamine to be the best suited additives. With an addition of urea to a binary $AlCl_3$—NaCl electrolyte containing 82 mass % $AlCl_3$ the value of $j_{cr}$ was increased to 120 mA cm$^{-2}$. It should be stressed, however, that such an increase was only obtained with an aluminium chloride concentration at the upper limit of the investigated concentration range.

More effective additives were found to be tetraalkylammonium halides, namely tetramethylammonium chloride (TMA) [59, 68]. An addition of 0.5—

2.0 mass % TMA to a ternary base electrolyte containing from 75 to 80 mass % $AlCl_3$ and from 20 to 25 mass % of a mixture of NaCl and KCl in 1 : 1 mass ratio allows the value of the $j_{cr}$ to be increased to 160—170 mA cm$^{-2}$, *i.e.* by about a factor of 3 to 4 compared with that obtained in the electrolyte without this additive. Still more important, the addition of TMA makes it possible to deposit coherent fine-crystalline silver-bright aluminium coatings from an electrolyte containing 70 mass % $AlCl_3$ at current densities of up to 70 mA cm$^{-2}$, *i.e.* comparable with (or even higher than) those used in the electrolytes without this additive and containing more than 75 mass % $AlCl_3$.

The quality of the aluminium coatings was estimated microscopically and using X-ray microanalyzer and a scanning electron microscope. The thickness of the deposits was determined gravimetrically and by the anodic dissolution method [56, 69]. The latter method made it possible to determine also the thickness of the diffusion underlayer. A direct determination of the thickness of the aluminium layer and underlayer on a cross-section of the cathode (coated substrate) by means of X-ray microanalysis revealed that the underlayer is only formed by a solid solution of Fe in Al without any intermetallic compounds [49] which is consistent with the literature data on diffusion in the system Fe—Al [47]. This composition of the diffusion layer guarantees a good bond between the base metal and the protective aluminium layer.

In order to elucidate the mechanism of the effect of the TMA additive on electrolytic aluminium-plating, some model systems similar to those used in the electrolysis were investigated by chronopotentiometry and sweep voltametry [80]. In the chronopotentiometric measurements, the addition of TMA did not produce any change in the shape of the potential response obtained when using an aluminium microelectrode. However, a distinct change in the current response was observed in the sweep voltametry measurements when inert microelectrodes (Pt and W) which did not react with the deposited aluminium were used. In agreement with data presented by *Rolland* and *Mamantov* [81] on other salt systems, it was concluded that the addition of TMA affects the initial stage of the electrocrystallization of aluminium, *i.e.* the formation of the crystallization nuclei. This conclusion is also supported by the results of an investigation of the effect of a TMA additive on the capacity of the electric double layer in the mercury—$NaAlCl_4$ and platinum—$NaAlCl_4$ systems [82]. Thus, it can be assumed that the complex $(CH_3)_4N^+$ anions, which are formed by the dissociation of TMA in the electrolyte, occupy (block) the active centres (sites) on the surface of the cathode (substrate). This process results in an energetic homogenization of the surface and consequently in an increased number of centres of crystallization. This assumption, however, requires further experimental confirmation.

## Effect of pulsating current

The assumption on the decisive part of electrocrystallization and, in particular of the formation of the crystallization nuclei in the aluminium-plating process stimulated research in which (i) the possibility of initiating the formation of a great number of Al crystallization nuclei on the surface of the substrate by initial current pulses and (ii) the possibility of suppressing the formation of dendrites by a systematic polishing (renewal) of the surface of the coatings by using the pulsating current in the course of the aluminium electrodeposition were examined [60, 70]. In both cases, rectangular pulses have been used. The ternary $AlCl_3$—NaCl—KCl mixture used as the base electrolyte contained 70—80 mass % $AlCl_3$ and 20—30 mass % of NaCl and KCl mixture (1 : 1 mass ratio). To this base electrolyte, 1 mass % TMA was added. Electrolysis was carried out at 180°C.

In the first series of experiments, a single initial cathodic current pulse with a current density, $j_c$, 3 to 8 times higher than the normal operating $j_c$ values was applied for 1 s in order to initiate the formation of an increased number of the crystallization nuclei and, consequently, the formation of a fine-grained aluminium coatings. The single current pulse, however, only exhibited a beneficial effect on the electrocrystallization of aluminium in very thin Al coatings (up to about 5 μm) and this effect vanished with increasing thickness of the deposited layer. Besides, the initial current pulse had almost no effect on the value of the $j_{cr}$ which was found to be within the range 70—160 mA cm$^{-2}$ depending on the concentration of $AlCl_3$ in the electrolyte.

More promising results were obtained with cyclic current pulses of alternating polarity. It was found that the duration of pulses should not exceed 10 s, the ratio of the duration of the cathodic and anodic pulses, $t_c$ and $t_a$, respectively, should preferably be within the range 3—5 and the ratio of the anodic and cathodic current densities, $j_a$ and $j_c$, should be preferably close to 2/3. Under these conditions, compact and fine-crystalline aluminium coatings were deposited at $j_c$ of up to 250 mA cm$^{-2}$, this value being independent of the electrolyte composition within the concentration range 70—80 mass % $AlCl_3$. With respect to the pulse technique used, the above value of the $j_{cr}$ corresponds to an average $j_c$ within the range 150—180 mA cm$^{-2}$, which means that the application of this technique to aluminium-plating would only be effective in electrolytes containing less than 75 mass % $AlCl_3$; these are, however, of a prime technological interest.

## Effect of a copper underlayer

Because the process of electrolytic aluminium-plating is essentially governed by the formation of crystallization nuclei of the new phase, it is evident that this

process depends also on the material of the substrate. It was found that on copper substrates, compact and silver-bright aluminium coatings were deposited at cathodic current densities of up to $180 \, A \, cm^{-2}$ regardless of the electrolyte composition within the range 70—80 mass % $AlCl_3$ [60]. An attempt was therefore done to deposit aluminium on copper-coated steel substrates. The thickness of the galvanically deposited copper layers was varied from 0.2 to 4 μm and it became evident that even a copper underlayer of 0.2 μm makes it possible to deposit compact aluminium coatings in an electrolyte with a composition close to the lower limit of the $AlCl_3$ content (70 mass %) at current densities comparable with those used in the current-pulse technique.

The aluminium deposition on copper-plated steel substrates was carried out over a wide range of cathodic current densities and it was found that the size of the Al crystals in the coating decreases with increasing $j_c$ which suggests that the plating should be carried out at high current densities to obtain compact fine-crystalline coatings.

Although the aluminium electrodeposition on a copper underlayer appeared to be the most promising process for aluminium-plating of steel substrates, it was found to be a failure as the corrosion tests proved the Al coatings deposited on a Cu underlayer to be clearly inferior to those deposited directly on steel. This obviously is due to a different structure of Al layers deposited on the respective substrates. The lamellar aluminium coatings deposited on steel exhibit a higher corrosion resistivity than the granular coatings deposited on copper which are open to intergranular corrosion.

### Effect of operational parameters

Based on literature data [49, 59—62], the following conclusions could be formulated on the effect of the operational parameters on the current efficiency of the process as well as on the critical thickness, the morphology and the texture of the aluminium deposits. (These conclusions hold for an electrolyte containing 1 mass % TMA).

(i) The current efficiency of aluminium deposition depends strongly on the cathodic current density. In general, when $j_c$ is increased the current efficiency (referred to the compact aluminium layer including diffusion underlayer) decreases, this effect being more pronounced at low concentration of $AlCl_3$ in the electrolyte. The dependence of current efficiency on current density indicates that the formation of the aluminium coating is governed by the kinetics of aluminium electrocrystallization.

(ii) The thickness of the aluminium coating increases linearly with the time of electrolysis at a constant current density up to a certain critical value ($j_{cr}$),

after which aluminium is deposited in the form of dendrites and/or powder. It was also found that the growth of an aluminium coating is accompanied by a steady increase in the size of the aluminium grains on the surface which eventually results in the formation of aluminium dendrites or powder. The thickness of the aluminium coating should be from 8 to 10 μm to guarantee a safe corrosion protection.

(iii) The morphology of the aluminium deposit is strongly dependent on the cathodic current density. In general, the grains formed at higher current densities are smaller and more isometric than those deposited at low current densities which supports the postulate of the governing role of the formation of crystallization nuclei in the process of the electrocrystallization of aluminium. (The same effect of $j_c$ on the morphology of Al deposits has been observed in aluminium-plating of copper-coated steel substrates — see above.)

(iv) In the temperature interval investigated (160—200°C) no temperature effect on the morphology of the deposited aluminium coatings was observed.

(v) The aluminium deposits are textured, and (200) and (111) crystal surfaces parallel to the surface of the substrate are preferentially developed. The texture vanishes as the thickness of the aluminium layer increases.

*Continuous aluminium-plating*

A bench-scale line for continuous aluminium-plating of iron (steel) wire has been assembled [62] in order to demonstrate the potential technological applicability of this method.

The electrolyte contained 71 mass % AlCl₃, 14 mass % NaCl, 14 mass % KCl, and 1% TMA. The electrolysis has been carried out at 180°C using a soluble aluminium anode.

The $j_{cr}$ values in continuous electrolysis were found to be essentially higher than the value corresponding to the above electrolyte in the stationary laboratory electrolysis (70 mA cm⁻²) and ranged within 100—250 mA cm⁻² depending on the motion velocity of the plated wire. This increase of $j_{cr}$ is obviously due to the stirring effect provoked by the motion of the wire in the electrolyte which stimulates the transport of the electrochemically active component (AlCl₃) to the surface of the cathode (wire).

The current efficiency of the plating process depends on the cathodic current density and mainly on the motion velocity of the wire. With a sufficiently high motion velocity (depending on the construction of the plating line), an almost 100% current efficiency can be achieved even at current densities close to the upper limit of the $j_{cr}$ interval (250 mA cm⁻²) compared to the value of 70 mA cm⁻² determined for the employed electrolyte in the stationary electrolysis.

The deposited aluminium coatings were compact, fine-crystalline, silver-bright, and with a thickness of 8—10 μm they exhibited a high corrosion resistivity.

### Coating by refractory metals

In this chapter, the electrolytic coating by metals with a high melting temperature (*i.e.* over the melting point of iron — 1535°C) denoted as refractory metals will be discussed. This category includes metals of groups IV B (titanium — (1660 ± 10)°C, zirconium — (1852 ± 2)°C, hafnium — (2227 ± 20)°C), V B (vanadium — (1890 ± 10)°C, niobium — (2468 ± 10)°C, tantalum — 2996°C), and VI B (chromium — (1857 ± 20)°C, molybdenum — 2617°C, tungsten — (3410 ± 20)°C)*. Besides outstanding physico-mechanical properties, the refractory metals generally also exhibit a high chemical stability in corrosive media which makes them attractive from the point of view of the surface protection of common metals, namely of steels.

From these metals, only chromium coatings have been deposited from aqueous solutions. The electrochemical deposition of refractory metal coatings has been pioneered by *Mellors* and *Senderoff* [84—94] who succeeded in depositing a series of refractory metals (Zr, Hf, V, Nb, Ta, Mo, W, Cr) from molten electrolytes except, however, for titanium.

Owing to its properties, the metallic titanium is widely used in the aerospace, marine, desalination, chemical and electronic technologies. It may be assumed that in some applications for the sake of economy the titanium-plated steel substrates can be used instead of pure titanium**.

Although titanium-plating cannot be considered — with respect to the electrolyte composition — to be a typical example of the coating by refractory metals, it will be dealt separately due to its potential technological significance while for the other refractory metals the literature data will be concisely surveyed.

### Titanium-plating

Numerous papers dealing with the electrolytic deposition and refining of titanium published over the last 30 years indicate a continuous interest of both

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* The melting temperature data are those recommended in [83].

** The same assumption holds also for the coating by the metals of the platinum group which is not discussed in this paper. Relevant references may be found in the review by *Sethi* [6].

scientific and industrial research in this topic. This interest is stimulated mostly by the rather poor economy and technological drawbacks of the present metallothermic process for the production of titanium based on the chemical reduction of titanium(IV) chloride either by molten magnesium (Kroll method) or sodium (Hunter method). Although the electrolytic process made a significant progress during the last two decades, it is reported (cf. Ref. [3] and [95]) that it did not extend beyond a pilot plant scale thus far. The published data reviewed recently by *Lovering* and *Williams* [3] are of importance also with respect to the titanium-plating.

In this chapter, the surveys on titanium-plating by *Matiašovský et al.* [4] (1972) and by *Sethi* [6] (1979) are updated and the relevant data are critically analyzed.

As a typical transition metal, titanium exhibits in its compounds several oxidation states: Ti(IV), Ti(III), and Ti(II). From the point of view of the electrodeposition of titanium metal, the titanium halides, namely chlorides and fluorides are of interest. They cannot be, however, electrolyzed directly owing to the unsuitable physicochemical properties. This can be demonstrated on the series of titanium chlorides [83]: $TiCl_4$, a typical covalent compound, melts at $-25\,°C$ and is virtually a non-conductor; $TiCl_3$ decomposes at $440\,°C$. The data on $TiCl_2$, a compound with an expressed ionic character, are rather controversial: According to [83], it sublimes in hydrogen and decomposes in vacuum at $475\,°C$. On the other hand, the melting temperature of $TiCl_2$, read from the phase diagrams of the systems $NaCl—TiCl_2$ [96] and $KCl—TiCl_2$ [97], is about $1025\,°C$, while according to [98], it sublimes in vacuum $(1.85\,kPa)$ at $(1035 \pm 10)\,°C$. (It should be mentioned that in [98] also the thermodynamic data for titanium subchloride, TiCl, are presented). The best solvents of titanium halides were found to be the molten alkali halide mixtures dissolving titanium halides under formation of various complex compounds depending on the valency of titanium and the composition of the alkali halide bases.
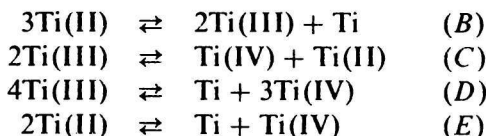
Considering the nature of the electrochemically active species, the electrolytes tested in the titanium-plating can be divided into three groups:
   (i) Electrolytes containing chloro complexes of titanium
   (ii) Electrolytes containing complex $TiF_6^{2-}$ anions
   (iii) Electrolytes containing $TiO_2$

Most interest was paid to the all-chloride electrolytes containing the chloro complexes of titanium dissolved in molten alkali or alkaline earth chlorides. The reduction sequence $Ti(IV) \rightarrow Ti(III) \rightarrow Ti(II) \rightarrow Ti(0)$ was investigated in a series of alkali and alkaline earth chlorides and mixtures by *Chassaing et al.* [99 —101] who found that for bases with a cation larger than $K^+$ the complexes of Ti(IV) and Ti(III) are stable while the solutions rich in Ti(II) are present in

melts containing cations smaller than $K^+$ (*e.g.* in NaCl or in the LiCl—NaCl —KCl eutectic mixture).

In this context also the disproportionation reactions

$$
\begin{array}{rcll}
3\mathrm{Ti(II)} & \rightleftarrows & 2\mathrm{Ti(III)} + \mathrm{Ti} & (B) \\
2\mathrm{Ti(III)} & \rightleftarrows & \mathrm{Ti(IV)} + \mathrm{Ti(II)} & (C) \\
4\mathrm{Ti(III)} & \rightleftarrows & \mathrm{Ti} + 3\mathrm{Ti(IV)} & (D) \\
2\mathrm{Ti(II)} & \rightleftarrows & \mathrm{Ti} + \mathrm{Ti(IV)} & (E)
\end{array}
$$

in the respective electrolytes which may be responsible for the formation of the titanium powders and the rather low current efficiency are considered.

Probably the first attempt to deposit titanium coatings from molten salts was made by *Cordner* and *Worner* [102] who electrolyzed $TiCl_3$ dissolved in the LiCl —KCl eutectic mixture at 550°C and a cathodic current density of 6 A cm$^{-2}$ using a tungsten cathode. At those conditions, however, only titanium powder was deposited with a current efficiency of about 60%. On the other hand, *Brenner* and *Senderoff* [103] succeeded in depositing titanium coatings with a thickness of about 12.5 μm on a thungsten substrate from a $TiCl_3$—NaCl—KCl electrolyte at 900°C and the cathodic current density of 0.3 A cm$^{-2}$.

Electrolysis of Ti(IV) chloride presented several problems, partially due to the low solubility of $TiCl_4$ (added as gas) in alkali chlorides. The most important step was found to be the reduction of Ti(IV) to the lower oxidation states [104 —106] which requires the utilization of a diaphragm in order to prevent the reoxidation of Ti(II) and Ti(III) to Ti(IV) at the anode.

*Alpert et al.* [104, 106] used a perforated cathode to introduce $TiCl_4$ into the NaCl—SrCl$_2$ eutectic mixture. After a partial reduction to Ti(II) and Ti(III) containing species (700°C, 2 mA cm$^{-2}$), these were reduced (at 10 mA cm$^{-2}$) on a solid cathode to crystalline coatings. The electrolysis has been carried out in an inert atmosphere with no traces of humidity or oxygen. Less successful has been the attempt by *Burgess et al.* [105] to reduce $TiCl_4$ dissolved in a NaCl —KCl mixture at 725—750°C and a cathodic current density between 1.5— 6.0 A cm$^{-2}$ under hydrogen. Under those conditions only dendritic titanium was deposited.

As materials for the diaphragm, cobalt, nickel as well as their alloys or iron substrates coated by Co or Ni were recommended [107, 108]. Here it should be mentioned that electrolytic reduction of $TiCl_4$ without a diaphragm, based on an original construction of the cathode assembly, was suggested by *Relisle et al.* [109].

According to *Baimakov* and *Vetyukov* [95], *Bockris et al.* [110], and *Menzies et al.* [111], the formation of the titanium powder in electrolytes containing Ti (IV) and also Ti (III) chlorides can be explained by the primary deposition of alkali metal which may take part in the electrolytic process depending on the

concentration of titanium, the activity of the alkali metal(s), the temperature and stirring of the electrolyte. The deposited alkali metal dissolves in the electrolyte and reduces the titanium ions in the proximity of the cathode under formation of a fine titanium powder. This mechanism of the cathode process, however, is improbable in electrolytes containing Ti (II) compounds due to the large difference between the deposition potentials of both metals (*e.g.* for the LiCl—NaCl—KCl—TiCl$_2$ mixture at 600 °C the values $E(Ti^{2+}/Ti) = 2.84$ V and $E(Na^+/Na) = 3.32$ V *vs.* a chlorine reference electrode were reported [112]).

The effect of the average valency of titanium ions in the electrolyte on the quality of the deposited titanium coatings was investigated by *Alpert et al.* [104, 106] who recommended the value of about 2.2. The favourable influence of an increased concentration of TiCl$_2$ is supported also by *Elyutin et al.* [113] who claims that it makes it possible to increase the current density and the thickness of the deposited Ti coatings.

*Ivanovskii et al.* [114] investigated the electrodeposition of titanium on a steel substrate (wire) in low-melting electrolytes based on lithium chloride (LiCl—KCl, LiCl—NaCl—KCl), cesium chloride (NaCl—CsCl, NaCl—KCl—CsCl), and magnesium chloride (KCl—MgCl$_2$, NaCl—KCl—MgCl$_2$) with equilibrium concentrations of the Ti (IV), Ti (III), and Ti (II) chlorides. Equilibrium has been achieved by exposing titanium metal to the electrolyte prior to electrolysis. Coherent and uniform titanium coatings with a thickness of up to 100 μm have been deposited from electrolytes containing LiCl and CsCl at cathodic current densities within 0.02—0.1 A cm$^{-2}$ while formation of dendrites was observed in electrolytes based on MgCl$_2$.

Numerous electrolytes containing Ti (II) and Ti (III) chlorides dissolved in various mixtures of alkali and alkaline earth chlorides (LiCl, NaCl, KCl, CaCl$_2$, BaCl$_2$, MgCl$_2$) have been suggested by *Tokumoto, Tanaka*, and coworkers [115, 116], *Tanaka et al.* [117], and by *Ogisu* and *Enomoto* [118]. The electrolysis has been carried out at 400—550 °C and cathodic current densities from 0.8 to 1.2 A cm$^{-2}$. Titanium coatings up to 0.5 mm thick have been deposited with a current efficiency between 50 % and 90 %. *Tokumoto* [119] also claimed Ti-plating from bromide electrolytes containing TiBr$_2$ and TiBr$_3$ dissolved in bromides of alkali and alkaline earth metals. The anodic and cathodic compartments were separated by a diaphragm.

According to *Filippova et al.* [120], thick (0.2—0.3 mm) and compact titanium coatings can be deposited on iron substrates from the electrolyte (LiCl—KCl)$_{eut}$ + 2—3 mass % TiCl$_3$ at current densities 0.08—0.15 A cm$^{-2}$ and temperatures from 400 to 450 °C.

The second group of papers and patents deals with the electrodeposition of titanium from electrolytes containing potassium hexafluorotitanate, K$_2$TiF$_6$, as electrochemically active component.

Probably the first attempt to deposit titanium from these melts was reported by *Brenner* and *Senderoff* [103] who electrolyzed $K_2TiF_6$—LiCl—KCl and $K_2TiF_6$—NaCl—KCl mixtures in an inert atmosphere at 850°C and cathodic current densities ranging from 0.3 to 1.0 A cm$^{-2}$. Under these conditions, however, only titanium powder was deposited.

More successful have been *Steinberg et al.* [121] and *Sibert* and *Steinberg* [122] who deposited titanium coating on an iron cathode from electrolytes containing 5—25 mass % $K_2TiF_6$ dissolved in halides of alkali and alkaline earth metals at 750—950°C and current densities within 0.5—5.5 A cm$^{-2}$ using a graphite or a soluble titanium anode. The thickness of the coatings achieved 125 μm and could be increased by repeated electrolysis. Special attention has been paid to avoid the traces of humidity and of oxidizing impurities.

The attempt to utilize a soluble anode of titanium carbide [123] in order to economize the Ti-plating process was rather unsuccessful as dendritic titanium with carbon inclusions was deposited.

All-fluoride electrolytes were suggested in patents [124, 125]. Besides, *Stetson* [124] recommended as electrolyte a mixture containing 50 to 90 mass % $K_2TiF_6$ and 10 to 50 mass % of alkali halides (LiF, NaCl, KCl). The electrolysis can be carried out at temperatures from 580 to 980°C, depending on the composition of the electrolyte, and at current densities from 0.02 to 0.8 A cm$^{-2}$. The thickness of Ti coatings on iron or Inconel bases was reported to be up to 1 mm. Lower cathodic current density (10 mA cm$^{-2}$) was recommended in the patent [125]. Here, Ti coatings with a thickness of about 75 μm were deposited on Fe, Cu, Ni, and Inconel substrates by the electrolysis of $K_2TiF_6$ dissolved in molten LiF—NaF—KF eutectic mixture (FLINAK) at 700°C.

*Matiašovský et al.* [4] and *Daněk* and *Matiašovský* [126] tested a series of electrolytes based on potassium hexafluorotitanate: $K_2TiF_6$, $K_2TiF_6$—NaCl, $K_2TiF_6$—KCl, $K_2TiF_6$—LiCl—KCl, and $K_2TiF_6$—NaF. In this research also the interaction of $K_2TiF_6$ with alkali chlorides has been investigated [127]. It was found that in the molten LiCl—KCl mixture a substitution of fluorine in $K_2TiF_6$ by chlorine takes place while in other mixtures this reaction does not occur. Titanium coatings with a well expressed crystallinity have been deposited from pure $K_2TiF_6$ at 900°C and cathodic current densities above 1.25 A cm$^{-2}$. The best results, however, have been achieved with the electrolyte containing 5 mole% $K_2TiF_6$ and 95 mole% NaF. In this electrolyte, homogeneous and uniform titanium coatings with a thickness from 5 to 50 μm were deposited at 1000°C and cathodic current densities within the range 2—4 A cm$^{-2}$ [128]. A good binding between the titanium coating and the iron substrate is ensured by the formation of the intermetallic compound, $Fe_2Ti$, in the underlayer [4, 122, 126].

In order to prevent the formation of dendrites, *Balikhin* and *Makarov* [129]

have used the pulsing current electrolysis. High quality titanium coatings up to 50 μm were deposited from a KF—LiF + 10 mass% $K_2TiF_6$ electrolyte at 750°C on Cu and Fe substrates alternatively polarized cathodically ($10\ A\ cm^{-2}$, 45 s) and anodically ($40\ A\ cm^{-2}$, 6 s).

Several attempts have been done to deposit titanium from electrolytes containing titanium oxides. Titanium powder contaminated by oxygen and carbon has been deposited by the electrolysis of TiO dissolved in halides of alkali and alkaline earth metals [130]. *Matiašovský et al.* [4] electrolyzed the system $Na_3AlF_6$—NaCl—$TiO_2$ which was investigated as an analogue to the aluminium electrolysis [131]. The cathode deposit, however, consisted of $TiO_2$ (as rutile). *Hashimoto et al.* [132] and *Hashimoto* [133] electrolyzed $TiO_2$, $MgTiO_3$, and $CaTiO_3$ dissolved in molten fluorides (NaF, $MgF_2$, $CaF_2$, $BaF_2$) at 1300—1850°C. The deposited titanium was contaminated by carbon and other impurities.

### Coating by other refractory metals

Data which may give fundamental information on the compositions of electrolytes and operating conditions which have been tested in the electrodeposition of refractory metals (except Ti) are summarized in Table 1. As may be seen, the recommended compositions in some cases are rather surprising and indicate the authors' claim for originality.

Based on an analysis of literature data reviewed by *Sethi* [6] and *Lovering* and *Williams* [3], the all-fluorides electrolytes are considered to be the best suited for deposition of refractory metal coatings. These electrolytes exhibit outstanding physicochemical properties of the alkali fluoride solvents (low melting temperature and vapour pressure, high electrical conductivity) and a high complex-forming ability with the refractory metal fluorides which is generally assumed to be the fundamental conditions for the deposition of dense and coherent coatings due to a reduced activity of the refractory metals complexed to the fluoride anions. The importance of the complex formation for the deposition of coherent zirconium deposits has been confirmed recently by *Kipouros* and *Flengas* [159].

The possibility of increasing the efficiency of the plating process by increasing the cathodic current density is limited by a certain threshold value denoted as the dendrite growth threshold current density ($j_{cr}$) (see chapter Aluminium-plating). In spite of a favourable influence of the presence of the complexes in the electrolyte, the possibility of increasing the $j_{cr}$ value is rather limited. *Cohen* [160] claims to have reached in the electrodeposition of niobium from molten fluorides an electroplating rate increase by a factor of about 10 by application of a

*Table 1*

Coating by refractory metals (except titanium)

| Metal | Electrolyte composition $w_i$/mass % | $\dfrac{\theta}{°C}$ | $\dfrac{j_c}{A\,cm^{-2}}$ | Substrate (Cathode) | Ref. |
|---|---|---|---|---|---|
| Zr | $(LiF—NaF—KF)_{eut} + 12—14ZrF_4$ | 680—800 | 0.005—0.03 | Mo | [87, 93] |
| Hf | $(LiF—NaF—KF)_{eut} + 8HfF_4$ | 600 | 0.005—0.1 | Cu | [93] |
|  | $(NaCl—KCl)_{min} + 6—7HfCl_4$ | 700 | 0.05—0.1 | Mo, Fe | [134] |
| V | $(LiF—NaF—KF)_{eut} + 10VF_3$ | 770 | 0.04 | Cu | [93] |
|  | $(LiCl—KCl)_{eut} + 5VCl_2$ | 400—450 | 0.01—0.02 | Mo, Ti, Ni, Fe, steel | [135] |
|  | $(LiBr—KBr)_{eut} + 6—8VBr_2$ | 400—450 | 0.01—0.02 | Mo, Ti, Ni, Fe, steel | [136] |
|  | $33NaBr + 37KBr + 22MgCl_2 + 8VBr_2$ | 400—450 | 0.01—0.02 | Mo, Ti, Ni, Fe, steel | [137] |
| Nb | $(LiF—NaF—KF)_{eut} + 16.2K_2NbF_7$ | 700—825 | 0.05—0.125 | Fe, Cu, Ni, C, steel | [84, 93] |
|  | $(NaCl—KCl)_{min} + 5—6NbCl_2$ | 700—720 | 0.05—0.2 | Fe, Cu, Ni | [138, 139] |
|  | $(NaBr—KBr)_{eut} + 4—10NbBr_3$ | 700—750 | 0.1—0.3 | Fe, Cu, Ni | [140] |
|  | $(NaI—KI)_{eut} + 4—6NbI_3$ | 700 | 0.1—0.2 | Fe, Cu, Ni | [141] |
| Ta | $(LiF—NaF—KF)_{eut} + 5—10TaF_5$ | 700—800 | 0.04—0.1 | Fe, Cu, Ni | [86, 93] |
|  | $(NaCl—KCl)_{min} + 7—10TaCl_4$ | 700—800 | 0.1—0.2 | Mo | [142] |
|  | $(NaCl—KCl)_{min} + 20K_2TaF_7$ | 750—800 | 0.05 | Mo | [143] |
| Cr | $(LiF—NaF—KF)_{eut} + 8CrF_3$ | 800—850 | 0.025—0.06 | Ni | [93] |
|  | $(NaCl—KCl)_{min} + 3.5—7CrCl_2$ | 800 | 0.025 | Ni | [144] |
|  | $(NaCl—KCl—NaF) + 5—20K_3CrF_6$ | 700—900 | 0.01—0.1 | Cu, Ni, Mo, Nb | [145] |
|  | $89.5AlBr_3 + 9.3KBr + 1.2CrCl_3$ | 220 | 0.02 | Fe | [43] |

*Table 1* (Continued)

| Metal | Electrolyte composition $w_i$/mass % | $\dfrac{\theta}{°C}$ | $\dfrac{j_c}{A\,cm^{-2}}$ | Substrate (Cathode) | Ref. |
|---|---|---|---|---|---|
| Mo | $(LiF—NaF—KF)_{eut} + 3—10MoF_3$ | 700—800 | 0.01—0.1 | Fe, Cu, Ni | [93] |
| | $(LiCl—KCl)_{eut} + 5—10K_3MoCl_6$ | 600 | 0.03 | W | [146] |
| | $(NaCl—KCl)_{min} + 5MoCl_3$ | 700—800 | 0.04—0.1 | C, W, Mo | [147—151] |
| | $83.5CaMoO_4 + 11.5CaCl_2 + 5CaO$ | 900—1000 | 0.05—0.1 | Fe, Ni, Cu, C | [152] |
| | $55.5NaBO_2 + 41.9LiBO_2 + 1Na_2MoO_4 + 0.9Li_2MoO_4 + 0.7MoO_3$ | 900 | 0.03—0.06 | Fe, Ni, Cu, C | [153] |
| W | $(LiF—NaF—KF)_{eut} + 10WF_6$ | 600—750 | 0.03—0.12 | C, Cu, W | [93] |
| | $90—96CsCl + 4—10Cs_2WCl_6$ | 750—800 | 0.03—0.05 | W | [154] |
| | $10CaWO_4 + 87CaCl_2 + 3CaO$ | 900—950 | 0.3 | Fe, Ni, Mo | [155, 156] |
| | $66.7LiNaB_2O_4 + 22.2LiNaWO_4 + 11.1WO_3$ | 900 | 0.01—0.03 | Ni | [157] |
| | $26.7NaBO_2 + 20.2LiBO_2 + 19.8Na_2WO_4 + 17.7Li_2WO_4 + 15.6WO_3$ | 900 | 0.04—0.06 | W, Mo, Ni, Fe, steel | [158] |

The symbols $\theta$ and $j_c$ denote the working temperature and the cathodic current density, respectively. The indexes eut and min denote the eutectic composition and the composition corresponding to the minimum on the respective liquidus curves.

periodic reversal technique, in which a cathodic (depositing) step is followed by an anodic (polishing) step.

### Diffusion coating

The diffusion coating, frequently referred to as "surface alloying", "metalliding" or "electrolytic cementation" differs from the metal-plating process as the deposited metals or non-metallic elements do not form a homogeneous surface layer with a constant composition through the thickness of the coating but diffuse fully into the surface of the substrate under formation of intermetallic or pseudo-intermetallic compounds and/or solid solutions. In comparison with the conventional cementation (hot dipping, gas or pack cementation process), the electrolytic cementation from molten salts can be carried out in a highly controlled manner as the rate of metal (element) deposition and the rate of metal diffusion into the substrate are independently controlled by changing the cathode current density and the temperature, respectively.

The electrochemical diffusion coating has been pioneered by *Cook* [161, 162] and *Ilyushchenko et al.* [163]. Although the electrolytes employed by Cook (all-fluoride melts) and the Ilyushchenko's group (chloride and chloride-fluoride melts) were different, the principle of the diffusion coatings formation has been essentially the same: Utilizing the difference in the positions of the substrate metal and the alloying element in the electrochemical potential series, the coating process proceeded spontaneously in a cell with a soluble anode of the more electropositive alloying element short-circuited externally with the less active substrate. The process continued until the activities of both electrodes became equilibrated. The application of an external current concurrent with the internal e.m.f. increased the rate of the coating formation by a factor of 3 to 10 [162] and made it possible to alloy the more reactive substrate metal with a metal with a lower electrochemical potential provided that the deposited metal diffuses readily into the substrate under formation of intermetallic compounds and/or solid solutions, thus lowering the activity of the cathode metal.

A great variety of diffusion coatings has been proposed in the open and in the patent literature with the aim to improve the corrosion and high-temperature oxidation resistance and/or to increase the surface hardness and the wear resistance of the surface-alloyed substrates. The typical alloying elements include Be, B, Al, Sc, Y, Si, Ge, Ti, Zr, V, Ta, Cr, Mn, *etc.* while the substrates involve a series of metals and alloys.

The general characteristics of the diffusion coating processes have been reviewed by *Galopin* and *Daniel* [5] and *Sethi* [6]. Recently the coverage has been expanded and updated to 1982 by *Kerridge* and *Lovering* [2].

In this chapter the results of the research into the boriding of steel substrates which has been extensively investigated in the authors laboratory will be presented and the data on siliciding will be concisely surveyed.

### Boriding

Boriding of metallic substrates, namely of steels, appears to be a highly effective method for increasing the surface hardness and wear resistance of various tools and machine parts. From literature data reviewed in monographs [164, 165] it follows that the boriding methods can be divided into two groups, depending on the way of saturation of the surface of the substrate by boron:

(i) Thermochemical boriding which can be carried out either in the gaseous phase or in a powder or molten boriding mixtures

(ii) Electrochemical boriding in molten electrolytes

The electrochemical process and the thermochemical boriding in molten salts have been found to be the most efficient boriding procedures. Although a higher rate of the boride layers growth can be achieved generally in the electrolytic process, the thermochemical boriding is often preferred owing to the technological simplicity and ability to coat uniformly intricate surfaces. Both procedures will therefore be surveyed in this chapter.

Based on the literature data [164—168] it was concluded that the mechanism of the boride layer formation in both cases is essentially the same: boron, deposited electrochemically or formed by the thermochemical reduction in the boriding mixture, diffuses into the substrate and reacts with the base metal under formation of borides. The thermodynamic activity of boron on the surface of the substrate, however, is generally higher in the electrochemical boriding, which results in substantial differences between the two methods as far as the kinetics of the boriding process (the rate of growth of the boride layer) and the phase composition of the boride layers are concerned.

From among various boron compounds, sodium tetraborate and potassium tetrafluoroborate were found to be the best suited for the *electrochemical boriding*. Although pure molten $Na_2B_4O_7$ [164, 169] and $KBF_4$ [170] have been successfully tested, polycomponent electrolytes are generally preferred as they exhibit improved physicochemical properties (liquidus temperature, vapour pressure, viscosity, electrical conductivity, *etc.*) compared to pure boron compounds. Alkali fluorides and chlorides are mostly used as supplementary components [164—168, 170—175]*.

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* The composition of the electrolyte is to be selected deliberately in order to prevent a possible deleterious reaction of components. Thus, *e.g.* it was found that in the systems of the type $KBF_4$—MCl (M = Li, Na, K) LiCl reacts with potassium tetraflouroborate under formation of gaseous $BCl_3$ while no analogous reaction was observed with either NaCl or KCl [176].

The choice of the respective electrolyte is determined by the operating temperature. Electrolytes containing $KBF_4$ as the electrochemically active component can be used within the temperature range 600 to 850 °C* while those based on $Na_2B_4O_7$ are operated at higher temperatures (750—1000°C).

Although repeatedly investigated, the mechanism of the cathode processes in the electrolytic boriding is not yet fully understood. *Yukin* [178] who investigated the mechanism of boron deposition in electrolytes based on $Na_2B_4O_7$ claims the primary product of the cathode reaction to be sodium which subsequently reacts with the components of the electrolyte in the proximity of the cathode under formation of elementary boron. The primary deposition of the alkali metal in the electrolysis of molten mixtures containing $KBF_4$ as the electrochemically active species has been suggested by *Cook* [161, 162] whilst, according to *Voroshnin* and *Lyakhovich* [1], the direct reduction of the $B^{3+}$ ions which may result from the dissociation of the $BF_4^-$ anions in the proximity of the electrolyte/cathode phase boundary cannot be ruled out. A simple 3-electron process was found to be the rate-determining step by *Brookes et al.* [175] in the investigation of the cathode reaction in the electrolytic boriding in fluoride melts. This has been confirmed recently by *Makyta et al.* [179] who investigated the mechanism of the cathode process in the electrolytic deposition of boron in the systems $LiF—KF—KBF_4$ and $LiF—KF—B_2O_3$, *i.e.* from electrolytes containing alternatively $KBF_4$ and $B_2O_3$ as electrochemically active components. It was found that in the system $LiF—KF—KBF_4$ boron is reduced directly from the tetrafluoroborate complex anion by a simple 3-electron process: $BF_4^- + 3e = B + 4F^-$. In the system $LiF—KF—B_2O_3$ boron oxide reacts with basic fluoride electrolyte under formation of the $BF_4^-$ anion and of unspecified oxofluoro complex(es). The difference between the deposition potentials of boron from those two electrochemically active species is about 0.47 V in favour of $BF_4^-$.

The cathodic current density employed in the electrochemical boriding varied from 50 to 500 mA cm$^{-2}$.

From an analysis of the literature data it follows that the process of the boride layer formation is controlled by the reactive diffusion of boron into the substrate. Consequently, the possibility of increasing the rate of this process by increasing the current density is limited by certain "critical" value at which the surface is saturated with boron (*i.e.* the thermodynamic activity of boron virtually equals 1) and the amount of the deposited boron corresponds to the

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* Although the phase diagrams of the $KBF_4$—alkali halide(s) systems suggest the potentiality to carry out the electrolysis at a temperature below the lower limit of the reported range (*e.g.* at about 500°C in the $KBF_4$—NaCl—KCl mixture [177]), this is virtually prohibited by a drastic reduction of the rate of the boride layer formation (see later).

amount of boron diffused into the substrate. The value of this critical current density is determined by temperature and the composition of the substrate (see later) which govern the diffusion process. Besides, the value of the $j_{cr}$ decreases with time as the growth of the boride layer slows down with increasing thickness of the layer.

It was also concluded that the composition of the electrolyte and the nature of the electrochemically active component do not affect the rate of growth of the boride layer and are only important with respect to the physicochemical properties of the melt (vapour pressure, viscosity, *etc.*) at the operating temperature.

From this analysis it is evident that there is a linear dependence between the thickness of the layer and the square root of the time of electrolysis, which is in agreement with the parabolic rule [180]

$$d = k \cdot t^{1/2} \qquad (1)$$

where $d$ is the thickness of the layer, $t$ is the time and $k$ is the proportionality constant. From this equation it follows that the square of the proportionality constant, $k^2$, has the dimensions of the diffusion coefficient, $cm^2 s^{-1}$, and describes the growth of the boride layer with a sufficient accuracy. Similarly as in the case of the diffusion coefficient, the temperature dependence of the squared proportionality constant $k^2$ can be adequately described by the Arrhenius equation

$$k^2 = k_0^2 \exp\left(-Q_d/RT\right) \qquad (2)$$

where the value $Q_d$ is often close to the value of the activation energy of diffusion. The value $Q_d = 175.5$ kJ mol$^{-1}$ [168] obtained for the low-alloy low--carbon substrate (see later) is several times higher than the average values of activation energies of diffusion, which is characteristic of diffusion process accompanied by a chemical reaction of the components.

In the *thermochemical boriding* process in molten salts, the boriding media containing a source of boron (mostly $Na_2B_4O_7$, but also another boron compounds such as $B_2O_3$, $KBF_4$ or $K_2B_4O_7$ [164, 165]) and a reducing agent (mainly $B_4C$ [164, 181], SiC [182, 183], metals or alloys [164, 165, 184, 185]) are employed*. Chlorides and carbonates of alkali metals are sometimes added to improve the physicochemical properties (mainly the temperature of the primary crystallization and viscosity) of boriding mixtures. The process is carried out at temperatures from 850 to 1050°C.
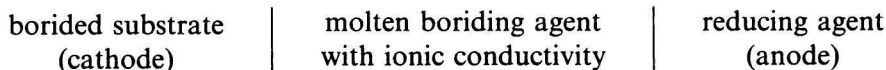
Contrary to the electrochemical procedure where the saturation of the surface can be ensured in such a way that the rate of the boride layer growth is only

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* It should be pointed out that in the thermochemical boriding instead of "pure" melts rather suspensions of the reductants in the boriding mixtures are employed.

governed by the diffusion of boron into the substrate and the formation of the boride phases, the activity of boron in the melt is of a definite importance in the thermochemical boriding.

The mechanism of the thermochemical boriding suggested in the monograph [164] is based on the assumption of the formation of a galvanic cell

| borided substrate | molten boriding agent | reducing agent |
|:---:|:---:|:---:|
| (cathode) | with ionic conductivity | (anode) |

where the driving force of the boriding process is the difference between the electrode potentials of the substrate and the reductant. This approach is close to the reaction mechanism proposed by *Cook* [161] based on electrochemical principles.

The mechanism of the boriding process with $Na_2B_4O_7$ as the source of boron and $B_4C$ and SiC, alternatively, as reducing agents has been recently investigated by *Makyta et al.* [186]. They found that when adding a reducing agent to molten $Na_2B_4O_7$, elementary boron is formed and it is dissolved in the melt. The activity of boron in the $Na_2B_4O_7$—$B_4C$ and $Na_2B_4O_7$—SiC systems substantially differs, depending on the nature of reductant, which may be used for preparation of boride layers with different phase composition.

The influence of the boriding conditions on the rate of growth and the phase composition of the boride layer has been recently investigated by *Chrenková et al.* [168, 187]. The electrolytic boriding has been carried out at $\theta/°C = 700, 750, 800, 850$, and 900 at a cathodic current density of $50$ mA cm$^{-2}$ which surpassed the $j_{cr}$ at all temperatures (*i.e.* with a boron activity on the surface of the substrate equal to 1). An electrolyte based on the LiF—KF eutectic mixture containing 10 mass % $KBF_4$ was utilized at temperatures from 700 to 800 °C while at higher temperatures a mixture of 80 mass % $Na_2B_4O_7$ and 20 mass % NaCl with a lower vapour pressure has been used. The thermochemical boriding has been carried out at 950 °C in mixtures containing alternatively 60 mass % $Na_2B_4O_7$ and 40 mass % $B_4C$ or 65 mass % $Na_2B_4O_7$ and 35 mass % SiC. Low-carbon low-alloy steel 1 (CSN 11 302: 0.06 % C, 0.17 % Si, 0.30 % Mn) has been used as substrate.

The boride layer formed electrochemically consists of two phases corresponding to the compounds FeB and $Fe_2B$. The two boride phases differ largely as regards their mechanical properties, namely the hardness (Table 2) and the brittleness (the surface FeB layer is harder and more brittle than the $Fe_2B$ underlayer). The observed root-like character of the boride layer is typical for this type of coatings.

The activity of the elementary boron on the surface of the substrate in the thermochemical boriding is generally lower compared with the electrolytic

process which affects both the phase composition and the rate of growth of the boride layer. Isolated "islands" of the FeB phase have only been formed over the $Fe_2B$ layer when using $B_4C$ as reductant and with SiC the formation of FeB has been entirely suppressed. In the latter case, however, the X-ray phase analysis revealed, besides $Fe_2B$, the presence of a new boride phase with a composition corresponding to the compound $Fe_3B$. The lower boron activity results also in a reduced rate of growth of the boride layer: the rate of the electrolytic boriding is by a factor of approx. 1.5 and 2.0 higher than in the thermochemical boriding in the $Na_2B_4O_7$—$B_4C$ and $Na_2B_4O_7$—SiC mixtures, respectively, in spite of a higher working temperature in the thermochemical process.

Extensive research has been carried out on the influence of various alloying metals on the boriding of steel substrates which is of prime technological importance. It was found that at low concentrations (up to about 2 mass%) most alloying elements only slightly affect the formation of the boride layer and only few (namely Mo and W) exert an inhibitory influence [164, 168, 187]. Thus in the boriding of the manganese steel 2 (CSN 19 312: 0.79% C, 0.40% Si, 2.00% Mn, 0.17% Cr) it was found that manganese does not affect either the rate of growth or the phase composition of the boride layer. A different picture, however, is obtained at high concentrations of the alloying elements [187]. The boride layer grown on the electrochemically borided high-alloyed chromium steel 3 (CSN 19 436: 1.85% C, 0.50% Si, 0.26% Mn, 11.25% Cr) exhibits a higher FeB content and apparently is more regular, $i.e.$ without distinctive "roots" on the boride layer/substrate interface. At the same time, the rate of growth of the boride layer is strongly reduced. This is assumed to be due to the accumulation of the expulsed chromium at the boride layer/substrate phase boundary under formation of a diffusion barrier which slows down the growth of the boride layer [187].

*Table 2*

Microhardness of boride layers grown on various steels

| Steel* | Microhardness/(N mm$^{-2}$) | | |
|---|---|---|---|
| | Substrate | Fe$_2$B layer | FeB layer |
| 1 | 1300 | 15 000 | 22 500 |
| 2 | 6500 | 15 000 | 22 800 |
| 3 | 7100 | 16 000 | 24 400 |

* The corresponding compositions are given in the text.

The values of the microhardness of the boride layers grown on the various steel substrates mentioned above are shown in Table 2. It may be seen that the

composition of the substrate only has a minor influence on the determined values. This stimulated the idea to overcome the difficulties encountered in the boriding of high-alloy steels by growing the boride layers on iron-coated steel substrates [188].

*Siliciding*

The silicide coating of various metallic substrates is one of the most efficient methods of forming hard surface layers with a good resistance to corrosion at both normal and elevated temperatures, especially to high-temperature oxidation. Siliciding can be carried out by cementation at high temperatures (1000 —1200°C) for relatively long periods (4—8 h), by chemical vapour deposition of silicon, or by electrolysis in molten electrolytes. Three different types of electrolyte have been recommended thus far:

(i) Mixtures of alkali fluorides containing an alkali hexafluorosilicate as the electrochemically active component [162, 189, 190]. The process is carried out at a temperature of about 700°C and current densities from 5 to 40 mA cm$^{-2}$, depending on the material of the substrate.

(ii) Silicate melts consisting of pure $Na_2SiO_3$ or a mixture containing 95 mass % $Na_2SiO_3$ and 5 mass % NaF [191]. In this case the electrolysis is performed in the temperature range 1000—1100°C at current densities generally by one order higher than in (i).

(iii) Electrolytes based on cryolite, $Na_3AlF_6$, containing silica as the electrochemically active component [192—194]. The mixture with the composition 90 mass % $Na_3AlF_6$ + 5 mass % $Al_2O_3$ + 5 mass % $SiO_2$ was found to be the best suited for siliciding. Electrolysis was carried out in a graphite crucible (anode) at 1020°C and cathodic current densities up to 250 mA cm$^{-2}$ in a protective atmosphere of dry argon or nitrogen.

In the application of $Na_3AlF_6$—$SiO_2$—$Al_2O_3$ mixtures to silicide coating, the possibility of a reaction between $SiO_2$ and $Na_3AlF_6$, which could lead to the formation of volatile $SiF_4$ is considered to be a problem of prime importance. It was found, however, that in the presence of alumina in the melt, the rate of this reaction was restricted and the above system may be considered stable [195].

*Fellner* and *Matiašovský* [193] investigated the possibility of the formation of silicide layers on a stainless steel (17.8 % Cr, 10.3 % Ni, 1.08 % Mn, 0.49 % Si, 0.12 % W, 0.20 % Cu, 0.60 % Ti, 0.08 % C, 0.024 % P, 0.016 % S) and on a Nimonic-type alloy (besides nickel: 15.5 % Cr, 9.0 % W, 4.0 % Mo, 3.0 % Fe, 1.4 % Ti, 0.16 % Si, 0.08 % C) which is used in the construction of moving parts, especially in gas turbines, from melts based on cryolite.

The experimental results obtained with a steel cathode support the assump-

tion that the rate of growth of the silicide layer is controlled by the diffusion of the deposited silicon into the substrate, the critical current density being within 200—250 mA cm$^{-2}$ at 1020°C. For the Ni-based alloys, the situation is somewhat different since nickel forms a silicide with silicon, NiSi, which melts at 992°C, the eutectic temperatures of the corresponding eutectics being still lower: 964 and 966°C [25, 196]. Hence it can be assumed that under certain experimental conditions a liquid phase is attained, at least temporarily. The correctness of this assumption was confirmed by results of the study of silicon deposition on a Ni cathode at current densities up to 1.0 A cm$^{-2}$ [197] which has been carried out within the research project directed towards the preparation of Al-Si alloys.

Although the X-ray phase analysis did not allow unambiguous determination of the silicide layer structure, it may be assumed that it consists of several intermetallic compounds which have been determined in the system Ni—Si [25, 198]. (The same holds for the silicide layers grown on the stainless steel).

The corrosive resistance of silicide layers was tested using a silicide-coated Nimonic alloy, a material used in mechanisms exposed to vanadium corrosion. Corrosion tests were carried out by exposing the silicided samples to molten $V_2O_5$—$Na_2O$ mixtures (70—90% $V_2O_5$) at 750°C for 2 h. From the corrosion tests it may be concluded that vanadium does not penetrate into the silicide layer. This confirms the positive influence of a silicide coating against vanadium corrosion where the couple V(V)/V(IV) may act as a strong oxidizing agent in the high-temperature oxidation.

### Multicomponent coatings

Recently the multicomponent coatings consisting mainly of borides, carbides and nitrides of the refractory metals deposited on various metallic substrates are gaining an increased technological interest because of their outstanding mechanical and/or anticorrosive properties [2, 6]. They can be obtained either by the electrodeposition of the respective metal on the substrate and the subsequent -iding process or by the electrochemical co-deposition and the simultaneous reaction of the components. The limited extent of this review, however, makes it impossible to discuss the possibilities of the multicomponent coatings which will be dealt with in a subsequent paper.

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