Translated from *Uspekhi Khimii* **60** 1077–1103 (1991) U.D.C. 621.357.12:546.62

Electrolytic deposition of metals on aluminium and its alloys

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ABSTRACT. The directions of the development of the technology of the deposition of galvanic coatings on aluminium and its alloys are examined. Attention is concentrated on the immersion method with preliminary contact segregation of metallic films, which has nowadays found the greatest practical application. Studies in the theory and practice of the electrodeposition of metals on preoxidised aluminium and also the direct deposition of galvanic coatings, whose main advantage is its universality and the simplicity of the technological process, are considered.

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I. Introduction

Among metallic constructional materials, aluminium has found extensive application. During the period 1950–1980, its world prodution increased almost by a factor of 12.[1] According to forecasts,[2] the requirement for aluminium in the year 2000 will increase by a factor of 4 compared with 1980. Thus multilayer copper–nickel–chromium and nickel–chromium (or binickel) coatings are deposited on it in the production of the protective, decorative trim. In order to protect the surfaces of articles against mechanical wear, thick layers of chromium are deposited and coatings consisting of lead–tin and copper–tin alloys are used to impart antifraction properties. In order to facilitate the welding of articles, use is made of tin–lead, tin–bismuth as well as nickel and silver coatings. The latter are employed to achieve contact and surface electrical conductivity in articles. Brass coatings are deposited on aluminium to facilitate the firm adhesion of its surface to rubber in hot pressing. Threaded aluminium articles are zinc-plated to prevent seizing. Protective cadmium and zinc coatings have been recommended for units where the aluminium components are coupled to components made of other metals in contact with which the corrosion of aluminium is intensified. Aluminium with coatings tinted to simulate "old bronze" or "old silver" are used in the making of artistic articles.[3–9]

However, aluminium has many properties which hinder the formation of high-quality metallic coatings on its surface. These include the high affinity of aluminium for oxygen, as a result of which its surface is rapidly covered by an oxide film in aqueous solutions, and the high negative potential of the activated surface which promotes the segregation of the contact metal. Furthermore, the possibility of the harmful influence of a number of physico-mechanical factors has been noted: such as the difference between the coefficients of the thermal expansion of aluminium and the metals deposited on it, the difference between their crystal lattice parameters, and the presence of hydrogen in the main metal and in the electrolytic deposits.[3,4,9,10] Different workers assess in different ways the importance of the above factors in particular situations. However, a decisive role is attributed to the first two factors: the presence on the coated surface of an oxide film, which prevents the firm adhesion of the coating to the base, and the negative potential of aluminium following its activation, as a consequence of which the corrosion of the metal constituting the base in electrolytes is accompanied by the formation of a porous, frequently powdery, contact deposit, which only weakly adheres to the aluminium surface.

As a consequence of the above difficulties, the attempts to treat aluminium using the same procedure as in the deposition of coatings on metals such as copper or iron have not led to satisfactory results. The electrolytic deposits had an unsatisfactory structure, adhered only weakly to the main metal, and did not meet other operating requirements. Special electrolytes and procedures for the treatment of the surface to be coated are therefore used to coat articles made of aluminium and its alloys. The general problems of the technology of the deposition of galvanic coatings on aluminium have been considered in a series of monographs and review articles.[3–5,8–17,etc.] In accordance with the nature of the preparatory operations and the surface obtained as a result of the preparation, the proposed methods for the deposition of coatings on aluminium are classified as follows:[4,11]

1) deposition of coatings on a rough surface;
2) deposition of coatings on a film of contact metal;
3) deposition of coatings on an oxide film;
4) direct method;
5) other methods.

However, the change in the state of the surface during the preparatory process cannot alone solve all the problems arising in the deposition of coatings on aluminium. Certain changes are in one way or another necessary also in the deposition stage. In a series of procedures, an additional heat treatment operation, usually for the coating of components, is also introduced into the technological scheme. The practical success of a particular process is determined by the extent to which account is taken in its individual stages of the

specific properties of aluminium and of the changes in these properties on passing from one alloy to another.

II. Deposition of galvanic coatings on a rough surface

The deposition of coatings on a rough aluminium surface is apparently the oldest method. The first studies date back to the beginning of this century.[3,4,9] The roughness of the coated surface is increased by mechanical, chemical, or electrochemical treatment. The adhesion increases as a result of the greater surface area of the cathode and the creation of additional bonding with the base as a result of the mechanical fixation ("anchoring") of the deposit in hollows on the surface. Solutions of hydrochloric, hydrofluoric, and chloroacetic acids or their mixtures with sulphuric, nitric, and phosphoric acids are usually employed for the chemical treatment. Electrochemical anodic etching is generally carried out in chloride solutions, sometimes with addition of other salts and acids. Sand blasting and hydroabrasive mechanical treatments are used to increase roughness.[3,4,17,18]

The systematic studies of this method[18–24] are associated with the development of electrochemical etching processes. It has been shown that electrochemical anodic dissolution ensures a greater number, compared with chemical dissolution, of etching sites on the aluminium surface and a greater uniformity of the etching.[20] Best results have been achieved using a hot (70–90 °C) solution of sodium chloride. The introduction of sulphates and tartrates into the solution leads, according to Batashov et al.,[20] to an increase in the ionic conductivity of the surface oxide and promotes the formation of a larger surface. The etching coefficient increases approximately by an order of magnitude and reaches 30–35, which makes it possible to obtain high quality, as regards adhesion, coatings of aluminium from the usual electrolytes: copper coatings from a pyrophosphate solution or nickel coatings from a sulphate solution.[18,20]

The method involving the formation of a rough surface, as an independent type of preparation of aluminium before the deposition of galvanic coatings, is nowadays finding a very limited application for the following reasons:[3,4,9,22,23]

1) insufficient reliability in ensuring a firm adhesion of the coating to the aluminium base;

2) difficulties in obtaining lustrous decorative coatings;

3) weak protective properties of rough coatings.

However, additional electrochemical or more often chemical etching in order to increase somewhat the roughness of the surface is frequently employed as an auxiliary operation in the preparation of aluminium and its alloys for coating by other methods.[5,24–26]

III. Deposition of galvanic coatings with an intervening film of contact metal

The deposition of a film of contact metal before the electrolytic deposition of coatings on aluminium is sometimes referred to as the immersion treatment or immersion preparation. The essential feature of the method is that aluminium is immersed in a corrosive solution containing the ions of a more positive metal M^{z+}. As a result of the action of the corrosive component of the solution (OH^- ions in an alkaline medium and F^-, Cl^-, and BF_4^- ions in an acid medium), the surface of aluminium is activated, the corrosion potential shifts in the negative direction, and a contact exchange reaction takes place:

$$zAl + 3M^{z+} \rightarrow zAl^{3+} + 3M.$$

One selects conditions such that the contact metal is segregated as a thin compact film and can serve as a base on which the galvanic coating is subsequently deposited.

The appearance of the immersion method is associated with the development of the chemical treatment method. In the early studies by Work, designed to achieve a rough surface by chemical methods, it was noted that certain etching solutions with a high content of a salt of a more positive metal not only make the surface of aluminium rougher but also form a contact film, which facilitates the electrodeposition process.[9] At the present time, there exist recommendations concerning the deposition of zinc, tin, nickel, copper, and other metal films. However, only some of them have found a wide-scale practical employment. The technological process involving the deposition of coatings includes the cleaning of the coated surface, the deposition of a film of contact metal, and the electrodeposition of the coatings. In some processes, provision is made for a concluding heat treatment.

The following factors which make it possible to obtain high quality galvanic coatings have been noted. When aluminium is immersed in a corrosive solution for the segregation of the contact metal, a passive film prevents the normal course of the deposition of the metal and the adhesion of the deposit to the base is removed from its surface. The contact metal protects the surface of aluminium against reoxidation. The etching of the aluminium surface in the course of the contact exchange is non-uniform, which results in an increase of its microroughness and improves the conditions for the preparation of coatings firmly adhering to the base. The principal disadvantage of the method is associated with the fact that the contact exchange process and hence the structure of the film depend on the composition of the alloy to be coated. In the deposition of films on different aluminium alloys, it is therefore necessary in many instances to alter the composition of the solutions, the conditions, and sometimes also the procedure for the preparation of the surface.

1. Alkaline solutions

OH^- ions are the strongest activators of aluminium. The activating capacity of alkaline solutions reaches maximum values at pH 15–16 (concentration of alkali 5–7 M). Under these conditions, the rate of the self-dissolution of aluminium at a corrosion potential of $-(1.4-1.8)$ V is 150–170 g $m^2 h^{-1}$.[27–29] The decrease in the rate of dissolution at higher concentrations of alkali is mainly attributed to the formation on the surface of the metal of solid aluminates or their hydrolysis products.[27] $[Al(OH)_4]^-$ is usually quoted as the final product of the overall aluminium dissolution reaction in alkalis:

$$Al + 4OH^- \rightarrow [Al(OH)_4]^- + 3\bar{e}.$$

Another formulation of this reaction, in which the final product is the anion AlO_2^-, can also be encountered. However, this form of formulating the reaction is more arbitrary, because the existence of the above species in aqueous solutions is regarded as unlikely.[30]

The study of the mechanism of the corrosion of aluminium in alkaline solutions has led most investigators to the conclusion that this process proceeds via a stage involving the formation of an

intermediate passive oxide or hydroxide film.[31–33] According to the results of Heusler and Allgaier,[33] in weakly alkaline solutions the film has the structure of bayerite while in strongly alkaline solutions it has the structure of hydrargillite, the rate of corrosion being limited by the process

$$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-.$$

The rate of self-dissolution remains constant within a wide range of potentials. The possibility of the dissolution of aluminium via an active mechanism even at very negative potentials is doubtful[34] and this term is frequently used merely to characterise the high rate of the process. Studies with the aid of rotating disc electrodes have demonstrated a significant influence of the diffusion factor—the supply of OH^- ions to the corroding metal—on the rate of dissolution. It has been suggested that contact films of zinc, tin, copper, and nickel be deposited on aluminium from alkaline solutions.

The commonest method of deposition of a contact metal film on aluminium is the zincate treatment. This method (it has been described in detail[3,9]) was proposed in the USA by Hewitson in 1927. In the USSR, the zincate preparation was first studied in detail by Lainer.[9] At the present time, most publications are devoted to this process. Wide-scale studies are being carried out on the mechanism of the zincate treatment process and new improved electrolytes are being proposed.[35,36]

The zincate treatment involves the immersion of the aluminium article in a solution of sodium zincate. In an alkaline solution of sodium zincate, the surface of aluminium is activated and a film of contact zinc is formed. In an alkaline solution, zinc exists in the form of complex ions and its deposition potential is very negative, which promotes the formation of a compact and thin contact film without deep etching of the main metal. Account is also taken of the favourable ratio of the crystal lattice parameters of the two metals.[3]

In the simplest case, the zincate solution consists of sodium hydroxide and zinc oxide. The thickness and compactness of the zinc film depend on the concentration of the solution, the ratio of the components, temperature, and the period during which the aluminium articles are maintained in the solution. Solutions containing from 5 to 100 g $litre^{-1}$ of ZnO are employed. In concentrated zincate solutions, it is easier to obtain high quality films. Such solutions do not require frequent changing or correction but their high viscosity hinders the washing of the surface and the treatment of articles with a complex profile. On the other hand, dilute ZnO solutions require more careful technological monitoring. The higher the concentration of OH^- ions, which form a complex with zinc, the smaller the thickness and the greater the compactness of the film. It is therefore recommended that a higher ratio of OH^- to zinc ions be maintained in dilute zincate solutions. With increase in process temperature and the exposure time, the thickness of the films increases. The process is generally carried out at room temperature. The duration of the treatment depends on the composition of the coated alloy. For an inadequate exposure, there is insufficient time for the contact coating to cover the main metal and, when the exposure is too long, a thick loose film is produced.[9]

An advantage of the zincate treatment is that it is possible with its aid to coat articles made of both pure aluminium and its alloys. The solutions employed are simple in composition and are cheap. The principal disadvantages are associated with the high percentage of rejects, because of poor adhesion of the coating in the treatment of many alloys,[5,37] and with the low corrosion stability of the zinc film.[3,38,39] In order to obtain a film firmly adhering to the base, careful maintenance of the treatment conditions is required. Best results are obtained on alloys containing copper and manganese. On high-silicon alloys (more than 12% of silicon), it is not possible to achieve a satisfactory adhesion.[9] According to the literature,[8,38] the greatest wastage is on alloys containing electronegative metals: zinc and particularly magnesium. In such cases it is recommended that the treatment be carried out in other contact zinc-plating solutions.[8] The low corrosion stability of the aluminium–zinc–galvanic coating system is associated with the fact that the zinc layer behaves in most cases as the anode both in relation to the coating and to the main metal. In the presence of perforating pores in the coating, the zinc film begins to dissolve vigorously in the first place exerting a protecting effect against the corrosion of the base and the coating. The corrosion of zinc leads to the swelling of the coating caused by the corrosion products.[38,39] Studies carried out to improve the zincate preparation are designed to eliminate the above disadvantages.

The main aspect of the improvement of the zincate treatment consists nowadays in the use of modified zincate solutions, which contain modifying additives: iron, nickel, copper, cobalt, lead, and other metal salts and nitrates, sulphides, and cyanides. The addition of metal ions improves the corrosion properties and structure of the zinc film, as a result of the latter becoming alloyed. Organic compounds are also introduced into zincate solutions: amines, acids, alcohols, and others. A correlation has been noted between the quality of the film and the corrosion potential difference between the film and the coated alloy in the zincate solution. The lower this difference, the sooner should the zinc displacement process be completed and the denser and thinner the zinc film. Although this postulate cannot be regarded as rigorous, it usually holds.[8] It has been shown[40] that, under the conditions of diffusion-dependent limitations, a loose zinc film is formed, whilst under the conditions of kinetic limitations to the rate of the process a compact film is produced. In the presence of modifying agents, the initial potential difference between the zinc film and aluminium diminishes and in the course of the contact treatment it approaches zero, which leads to the retardation of the contact exchange in the course of time. In modified zincate solutions a rigorous maintenance of the duration of the operation is therefore not required and it depends less on the type of alloy to be coated.[41] At the same time, the small potential difference between the zinc film and the aluminium base in the modified solutions, in the treatment of alloys containing magnesium and zinc, leads to the need for additional cathodic polarisation of the aluminium components in the zincate bath.[38]

One of the first most successful modified zincate solutions contains added iron(III) chloride and a tartrate salt.[9] The zinc film deposited from this solution contains a small amount of iron, which increases the corrosion resistance and compactness of the film. The tartrate salt binds the iron ions into a complex, preventing their precipitation in the alkaline solution, and also regulates the rate of formation of the deposit and its structure. The solution can be used to coat alloys which are coated unsatisfactorily in the unmodified zincate solution. Very satisfactory results have been noted for alloys containing magnesium or both magnesium and silicon.

Modified zincate solutions containing copper and nickel complexes (mainly cyanide complexes) have come to be most widely used abroad in recent years. It has been noted that these additives regulate the potential difference between the aluminium alloys and the zinc film,[41] diminish the thickness of the film,[36,42] improve the

lustre of the electrolytic metal deposits,[36,43] and appreciably increase the strength of the adhesion of the coating to aluminium.[36,42,44] Copper and nickel are also effective alloying components which increase the corrosion resistance of the films.[36] For example, in the "Bondal" process, the compact deposit consists of 86% of zinc, 8% of copper, and 6% of nickel, while in the "Bettel" process it consists of 90% of zinc, 5% of copper, and 5% of nickel.[36] It has been noted[38,42,45] that zincate solutions modified by copper and nickel cyanides can be used to coat aluminium alloys containing silicon, magnesium, and zinc.

Organic components are sometimes introduced into the zincate solutions. A wide range of organic additives, functioning as complex forming ligands and surfactants, have been investigated.[3,46] Organic additives make it possible to use more economical dilute zincate solutions and ensure the formation of a thin, compact zinc film strongly adhering to the base.

In a series of technological processes using the zincate method for the preparation of aluminium, provision is made for the treatment of the articles after the deposition of the electrolytic coatings. The influence of such treatment on the quality of the coatings has been investigated by Lainer.[8] Lainer attributes the increase in the strength of adhesion during the heat treatment to the formation of a diffusion layer at the main metal–coating interface. A temperature of 200–250 °C and a treatment time of 30 min are recommended as the optimum conditions for the heat treatment in the nickel plating of aluminium.

Coatings with a more stable quality are obtained in the double zincate treatment of aluminium. It involves the removal of the contact zinc film from the article in nitric or sulphuric acid solutions and the retreatment of the article in a zincate solution. The potential difference between the base and zinc in the case of the double zincate treatment is smaller than in the single treatment. A thinner and denser film is obtained. The process was first investigated by Edwards and Swanson.[47] At the present time, this procedure is applied widely when both the usual and modified zincate solutions are employed.[5,43,48,49] It has been noted that in a number of instances, when after the single treatment the coatings adhere inadequately to the base, the double zincate treatment yields satisfactory results. In some instances, the double zincate treatment ensured the same strength of adhesion of the coating to the base as the single treatment with subsequent heat treatment.[9,50] According to Ref. 51, the use of the double zincate treatment makes it possible to obtain a strength of adhesion which is not inferior to the strength of the main metal. The disadvantages of the double zincate treatment are the increase in the number of technological operations and the additional consumption of reagents.

Aluminium articles coated by a zinc film are frequently copper-plated and electrolytically and chemically nickel-plated; chromium, cadmium, and silver plating as well as coatings consisting of other metals are used more rarely. For the deposition of electrolytic and chemical coatings on a zinc film, both the usual universal electrolytes and special electrolytes yielding better results are employed. These electrolytes are less corrosive to the thin zinc film, which is easily damaged and decomposed in many solutions. The film is deposited immediately after the zincate treatment and careful washing of the components. It has been noted that[52,53] even a short exposure of components with a zinc film to air can reduce greatly the strength of adhesion. The characteristics of a set of special electrolytes are presented below.

Weakly alkaline cyanide electrolytes with pH < 10 having an increased content of free cyanides and added tartrates are recommended for copper plating. It is also recommended that the components be immersed in the electrolyte with current flowing as well as an initial current pulse.[4,5,36,54]

Special electrolytes have been recommended for the deposition of thin electrolytic nickel coatings ("overcoats") on articles with a zinc film. Electrolytes containing citrates, which inhibit the contact exchange between the film and the nickel-plating electrolyte, have been proposed.[8] However, citrate electrolytes are expensive and unstable. Sulphate electrolytes, whose pH is in the range from 5.3 to 5.7, are more convenient for practical use. The electrolysis is carried out at 18–25 °C and at a low cathodic current density (0.5 A dm^{-2}).[52] The chloride-free sulphate matt nickel-plating electrolyte is recommended[55] for the covering of a zinc film by a thin (approximately 1 μm thick) nickel layer. An acetate-glycolate electrolyte, in which Ni^{+} ions are bound in the complex with glycollic acid, has been proposed for the deposition of a thin (2–3 μm) layer of nickel. It differs from sulphate solutions by being less corrosive and less stringent requirements have therefore to be met by the quality of the zinc film.[22,53] The electrolyte has been used successfully for the deposition of electrolytic coatings on aluminium in automatic apparatus. The mechanism of the deposition of nickel on a zinc film from such an electrolyte has been considered.[56]

As noted by Schmeling,[57] the zincate treatment is the most reliable procedure for the preparation of aluminium before chemical nickel plating. In this case, relatively non-corrosive weakly acid and weakly alkaline solutions are used for the deposition of nickel.[55,57–60] In order to reduce the corrosiveness, nickel is introduced in the form of acetate and a large amount of ligands, for example, citrates[59] or lactates,[60] is introduced. When aluminium components with a zinc film are immersed in a chemical nickel-plating solution, the nickel deposition process does not begin immediately. The induction period, lasting usually 10–20 s, is caused by the negative potential of the surface of the component (about −0.75 V), which arises on dissolution of the zinc film. The dissolution of zinc is accompanied by the contact liberation of nickel and the gradual displacement of the potential into the positive region as far as −(0.4–0.45) V (depending on the composition of the aluminium alloy, the thickness of the zinc film, and the composition of the chemical nickel-plating solution). The potential stabilises at this value and the chemical nickel-plating process begins.[58–61]

It has been established[58–61] that the zinc film dissolves almost completely in the chemical nickel-plating solution, but most of the dissolved zinc is subsequently chemically reduced forming the so called "zinc-enriched layer". The thickness of this layer varies from 50 to 300 nm. At the same time, the correlation between the thickness of the "zinc-enriched layer", on the one hand, and its zinc content and its adhesion, on the other, has not been observed. In order to increase the reliability of the adhesion of chemical nickel coatings, it is recommended[55] that, after the zincate treatment, the components be activated for 10–15 s in very dilute sulphuric or sulphamic acid solutions.

Analysis shows that the zincate treatment is widely used both in the USSR and abroad. This procedure is proposed as the main method or one of the main methods for the preparation of aluminium and its alloys before the deposition of electrolytic coatings in modern textbooks of electroplating,[8,62,63,etc.] in monographs,[3,4] in review articles on the coating of aluminium,[48,64–66,etc] and in the Standards of the USSR,[67] the USA,[65] and other countries. The compositions of modern zincate solutions are not as

a rule fully revealed by foreign firms. The solutions are prepared from compositions made up by the producer firm in a dry form or in the form of concentrated solutions.[48] The "Bondal", "Bettel", "Persal", and other processes have found extensive applications. At the same time, the disadvantages of the zincate treatment noted above have stimulated studies designed to devise other processes. This trend is particularly characteristic of the Soviet Union, where the number of studies on the zincate treatment since the 1950's has diminished sharply and the efforts of investigators are concentrated on the development of new technological processes.

In the 1960's, treatment in another type of alkaline solutions (stannate solutions) began to be applied—here aluminium components are coated by a film of contact tin. These films have been mainly used as independent coatings for the improvement of the antifriction properties of the aluminium surface.[3,9,68] The first communications[69,70] concerning the successful use of the stannate treatment before the deposition of electrolytic coatings on aluminium date back to 1964–1965.

The technological process for the coating of aluminium using the stannate treatment includes the cleaning of the aluminium surface by traditional methods, contact treatment in the stannate solution, coating with bronze in a cyanide electrolyte, and copper plating in a cyanide bath.[41,48] In order to avoid the hydrolysis of stannate in the film of solution on the surface of articles, it is recommended that they be transferred to the bronze-coating bath without preliminary washing.[41,48,71] Stannate treatment processes ("Alstan 80" and "Alstan 80A"), in which the thin film is deposited electrochemically in a stannate solution, have appeared in recent years.[48]

Studies[72,73] have demonstrated an appreciable influence of the kinetics of the tin liberation process on the adhesion of the coatings. It has been noted[73] that, in the stannate treatment, there is an initial rapid dissolution of aluminium induced by the high content of free alkali and the elevated temperature of the solution. During the first 10–20 s of the process, about 2000 aluminium atoms are dissolved per deposited tin atom. Subsequently this ratio is altered rapidly, reaching 1:6. At the same time the rates of dissolution of aluminium and of the evolution of hydrogen are reduced, which can be explained by the coverage of the main metal by the contact deposit of tin. The tin deposition process begins on the electropositive components of the alloy. The marked influence of impurities and alloy components on the stannate treatment process is responsible for the dependence of the conditions in the stannate treatment on the type of coated alloys.

Compared with the deposition of zinc from zincate solution, the contact deposition of tin from stannate solution is much slower and less uniform, while the films formed are thinner and more porous. In order to accelerate the deposition of tin and to increase the number of crystallisation centres, the aluminium particles in stannate solutions are sometimes subjected to additional cathodic polarisation. After coating with bronze and subsequent copper plating, the intervening layer between aluminium and copper consists of a tin-enriched bronze.[39]

Modern solutions for stannate treatment contain, together with the main components (sodium stannate and the free alkali), mixtures of additives, usually organic ligands and surfactants, which regulate the structure of the deposit.[74] The solutions used in the technological process are prepared as a rule from compositions supplied by the manufacturers. The commonest compositions are Alstan and Alstan 20 and 30 for the cleaning of the surface, Alstan 70, 75, 80, and 80A for the deposition of tin, and Alstan 71 for the electrolytic coating of tin by a layer of bronze.[39,42,75,76]

The main advantage of the stannate treatment over the zincate treatment is that it can be used to deposit coatings on articles employed under more severe climatic conditions. The tin film is more resistant to corrosion than the zinc film. However, more expensive and scarce reagents are used for the preparation of stannate solutions and the latter are relatively unstable, being hydrolysed, and therefore have to be changed frequently. The conditions in the stannate treatment also depend on the type of alloy coated. Thus, in the coating of aluminium–silicon and aluminium–magnesium alloys, such treatment yields unsatisfactory results. Although the stannate process produces contact films of higher quality, it is therefore recommended only in special applications where a high cost is justified.[39,41,77]

The stannate treatment has not found extensive applications in the USSR. Studies on the stannate treatment process have been carried out at the Academy of Sciences of the Lithuanian SSR and at the Leningrad Polytechnic Institute. The possibility of using pyrophosphate electrolytes in the stannate method for the electrolytic deposition of bronze and copper coatings has been demonstrated.[71,78]

Alkaline solutions are also recommended for contact deposition of copper and nickel films on aluminium, but their use is more limited compared with zincate and stannate solutions. In order to ensure the solubility of Ni^{2+} and Cu^{2+} compounds in an alkaline medium, an excess of ligands is introduced into the solution. It has been suggested in studies carried out in recent years that amines be employed as such ligands. An ammine electrolyte for the contact copper plating of aluminium and its alloys has been developed at the Kharkov Polytechnic Institute.[79,80] In this solution the OH^- ions have a decisive influence on the morphology of the deposit: at pH < 11.9, copper is hardly deposited, while at pH > 13.5 a dark, loose coating is produced. Thus the working pH range is 11.9–13.5. The optimum thickness of the copper deposit is 1.3–1.5 μm. The sublayer of copper ensures the firm adhesion of the subsequent electrolytic deposit to aluminium, although it can be used also as an independent coating. A similar electrolyte for the contact nickel plating of aluminium and its alloys has been proposed in the USA.[81] Ammonia and organic amines are used as ligands in this instance. The treatment is carried out at a pH of about 12 and at room temperature. According to the authors data, the contact nickel film ensures the effective adhesion of the subsequent electrolytic nickel coating to the base.

2. Acid fluoride and fluoroborate solutions

Aluminium dissolves in acid media also with formation of an intervening oxide film.[31] The activating capacity of H^+ ions is much lower than that of OH^-. According to the studies of Thomas and co-workers,[82,83] this factor can be explained by the fact that in the presence of H^+ only the hydroxo-groups forming part of the compositon of the surface oxide are highly reactive, the $Al-\underset{\displaystyle H}{\underset{|}{O}}-Al$ groups are stable, while the $Al-\underset{\displaystyle Al}{\underset{|}{O}}-Al$ oxo-groups are very stable. Anions may catalyse the aluminium dissolution process. Among them, fluorides are the most effective. In the presence of fluoride, the rate of dissolution of aluminium increases greatly, while the corrosion potential shifts to the negative region as far as −(1.2–1.35) V. The activating capacity of fluorides increases with increase in concentration but in highly concentrated solutions it falls again owing to the formation of a film of fluoroaluminates.[84] The intervening oxide film on aluminium also contains fluorides, whose

concentration diminishes from the outer surface to its barrier component.[85] According to Wiedmer and Grauer,[86] the rate of the dissolution is limited by the supply of the fluoride to the surface of aluminium and by the heterogeneous-phase interaction of the fluoride with the oxide.

Heiman[87] demonstrated the possibility of the contact deposition on aluminium of zinc, cadmium, tin, and copper films from fluoride-containing solutions and their use for the subsequent electrolytic deposition of other metals.

A new technology for the tinning of aluminium wire has been introduced. It involves the contact deposition on a pre-cleaned surface of the metal of a sub-layer of tin from a highly acid fluoride solution. The tin sublayer is coated with copper in a cyanide bath and the wire is then tinned in a fluoroborate electrolyte.[88] A technology for the tinning of aluminium wire has been developed and tested under semi-industrial conditions. Its main operations are the deposition of a film of zinc–nickel alloy from a weakly acid fluoride-containing solution, electrolytic copper plating in a pyrophosphate electrolyte, and tinning.[89] It was noted that both technologies ensure the formation of high quality coatings which withstand welding.

A series of fluorobroate solutions have been proposed for the contact deposition of zinc and its alloys with nickel. Fluoroborates are also effective activators of aluminium, being somewhat inferior in this respect to fluorides.[87] High quality deposits of contact zinc can be obtained from a solution of zinc fluorobrate at pH 3.0.[8] In order to improve the quality of the film, nickel and ammonium fluoroborates are added to the solution.[3,90,91] A solution proposed in a patent[91] is used in the Limeda Al biological process for the deposition of a zinc–nickel alloy film (30–40% of nickel) on aluminium. The articles are immersed in the solution initially without a current and then a brief electrodeposition of the alloy is carried out. In order to increase the strength of adhesion of the film to aluminium, it has been suggested that triethanolamine[92] or Sintanol DS-10[10] be introduced into the solution. It is recommended that, before the contact treatment, etching be carried out in a solution containing fluoroboric acid.[25] Electrolytic coatings can be deposited on the contact film of the zinc–nickel alloy from relatively non-corrosive electrolytes whose pH is in the range 4–10. Best results are obtained for copper plating in a pyrophosphate electrolyte and for nickel plating in a sulphate electrolyte.

By virtue of certain advantages over the zincate treatment, the Limeda Al technology has found applications in a number of undertakings in the USSR. The lower porosity of the film and the improved corrosion reistance of the coatings should be included among the advantages of this technology,[93–95] while its disadvantages comprise the more complex preparation and use of the solutions and also the need to maintain different treatment conditions for different aluminium alloys.[41]

The influence of various factors on the adhesion of electrolytic coatings to aluminium, treated in fluoroborate solutions for contact deposition, has been investigated in recent years.[95–101] According to the authors of these studies, the adhesion of coatings to the main metal is determined by the compactness of the structure of the contact film and is independent of its thickness. If the contact film is not continuous, then on the sections where it is absent the adhesion is unsatisfactory. On the other hand, on the sections where the zinc–nickel alloy film is in contact with the base, the strength of adhesion exceeds the intrinsic strength of aluminium. The adhesion can be impaired by partial etching of aluminium under the contact deposit caused by over-exposure to the fluoroborate solution or by the treatment with a corrosive electrolyte in the deposition of the coating.

3. Acid chloride solutions

Chlorides are effective activators of aluminium in an acid medium. According to the classification proposed by Davydov and Kamkin,[102] chlorides are anodic-anionic activators. In this case activation takes place as a result of the electrical breakdown of the passive film, which can occur even at stationary potentials of $-(0.4-0.65)$ V. It has been noted[103] that, for the activation mechanism indicated, there is a possibility not of a decrease of the thickness of the passive film but merely of an increase in its defectiveness. The latter factor leads to the local character of the dissolution of aluminium accompanied by an increase in the roughness of its surface. Chloride solutions have been proposed for the contact deposition of nickel, iron, manganese, copper, and a number of other metals.[3,9] The contact deposition of nickel on aluminium from a solution of nickel chloride in phosphoric acid has found the greatest practical application in the USSR.[104,105] The nickel film serves as a base for the subsequent chemical or electrochemical nickel plating. The corrosion resistance of the coatings deposited on contact nickel is much higher than that of the analogous coatings deposited on a zincate film.[106,107] However, the employment of the method on a wider scale is prevented by the inadequate reliability of the adhesion of the coatings to the base comprising certain alloys.[108] In a number of instances, it is altogether impossible to obtain high quality contact films. It has been shown that heat treatment improves the strength of adhesion of the coatings to the base.

Solutions for the contact copper plating of aluminium, containing chlorides as activators, have been investigated.[79,109–111] Thus an oxalate electrolyte, incorporating a small amount of chlorides, has been recommended for this purpose.[111] Copper deposits up to 5μm thick adhere satisfactorily to the base and can be used both as a sublayer for the subsequent deposition of electrolytic coatings and as an independent coating, for example, for welding.

IV. Deposition of galvanic coatings on oxidised aluminium

The method consists in the anodisation (sometimes chemical oxidation), after preliminary cleaning, of the surface to be coated followed by the deposition of the electrolytic coating. The process was developed in the 1930's mainly as a result of the studies of Fischer (quoted after Ref. 17), Travers,[112] and Kudryavtsev.[113] Phosphoric acid (more rarely oxalic, sulphuric, chromic, and other acids) is usually employed nowadays to obtain the anodic oxide, but mixtures of acids are also used.[3,17,24,60] Nickel, copper, cadmium, silver, iron, zinc, and chromium are deposited on the anodised aluminium.[11,17,114] Copper plating in a pyrophosphate electrolyte and nickel plating in a sulphate or sulphamate electrolyte are commonest. Apart from the operations indicated, the technological process sometimes involves additional etching before oxidation or after it[9,113,115–118] and a concluding heat treatment of the coatings.[119,120]

An advantage of the method is the improved protecting capacity of the coatings associated with the presence of an oxide film on the surface to be coated. A disadvantage is its high sensitivity to the smallest changes in the composition of the treated alloys. The purer the aluminium, the greater the difficulties arise in its coating. For pure aluminium, anodic treatment altogether fails to yield positive

results. Certain copper-containing and cast alloys are not always coated satisfactorily. The disadvantages of the process are its relatively high cost and the need to have for anodisation special power supply sources with an increased voltage.[3,9,10] For these reasons, the method is nowadays finding only a limited application compared with the immersion method.[48] Modern studies of the deposition of metals on oxidised aluminium are directed towards the investigation of the process mechanism and the improvement of the technology in order to eliminate the above disadvantages.

1. Mechanical theory of the adhesion of electrolytic metal deposits to oxidised aluminium

The commonest is the mechanical theory of the adhesion of an electrolytic deposit to the anodic oxide film. The foundations of the theory were laid by Keller et al.,[121] who noted the dependence of the structure of the anodic oxide on the composition of the anodisation electrolyte and a number of other factors and put forward the hypothesis that the structure of the anodic oxide is the determining factor in the deposition of metallic coatings on it. It was suggested that, since the films obtained in phosphoric acid are distinguished by the presence of numerous large-diameter pores, they should yield best results also on anodisation of aluminium before the deposition of electrolytic coatings on the latter.

The theory treats the anodic oxide as a dielectric having a discrete structure. During the deposition of coatings, the electric current passes mainly through "weak sites" in the oxide layer, which consists of pores, micro-cracks, and sometimes the inclusions of more noble metals. The electrolytic deposit begins to be formed initially within the pores as finely dispersed fibres, which then grow together, forming bridges across the film. Adhesion is achieved as a result of the mechanical fixation of the coating within the pores of the oxide film, which in turn adheres firmly to the main metal.[5,9,122] These postulates have been confirmed by a number of experimental data. At the beginning of the electrolysis, the formation of an electrolytic deposit is observed only at individual points on the cathode. Owing to the high true current density, the first layers of the metal in deposition on an oxide layer have a dark and even black colour regardless of whether copper, nickel, or silver is deposited and acquire the normal form only as the coating grows. According to data of Schardein[122] and Lashmore,[123] firm adhesion is achieved when the pores of the anodic film have been completely filled with the electrolytic deposit. The electrolytic deposits obtained in the pores under these conditions have the form of intertwined tree roots.[124,125] It has been established that the complete filling of the pores of the anodic oxide by the electrolytic deposit takes place in the deposition of coatings at low current densities, apparently owing to the elimination of diffusional limitations. It has been recommended in a number of publications[123,126,127] that, in the deposition of coatings on an anodic oxide, the cathodic current density be gradually and slowly increased (in the first minutes of the electrolysis) from zero to a stationary value. A correlation has been noted between the geometrical size of the pores and the quality of the coatings. It has been confirmed that the largest and most uniformly distributed pores are present in films obtained in phosphoric acid and this explains the finding that, when the latter is used, high quality coatings are obtained.[17,24,121]

It has been established[122] that the pore diameter increases with increase in the anodisation potential. At the same time an improvement in the adhesion of the coatings to aluminium has been noted.[122,123] However, the cathodic electrocrystallisation of metals on films obtained at very high potentials (60–80 V and above) is difficult apparently due to the appreciable thickness of the barrier layer. This feature together with the decrease in the total number of pores leads to a diminution of the number of centres for the electrocrystallisation of the electrolytic deposit and to a decrease in the strength of adhesion.[24,122]

High quality coatings can be obtained starting from a specific thickness of the anodic film.[24,123] For a small thickness (i.e. for a short anodisation time), the adhesion is unsatisfactory. Kishi[24] compares this kind of coating with a tree having weak, shallow roots. Lashmore[123] suggests that the side walls of the pores make the main contribution to adhesion. With increase in the thickness of the anodic film, the lateral surface of the pores increases and thus ensures the necessary strength of adhesion. For a greater thickness of the oxide film, the electrodeposited coatings become non-continuous as a result of the decrease in the number of crystallisation centres.[24,128,129] This phenomenon is usually observed for anodic films obtained in sulphuric acid.

However, certain experimental results cannot be explained satisfactorily on the basis of the mechanical theory of adhesion. According to a number of workers,[24,123,128,129] the difference between the structures and pore sizes of the films obtained in phosphoric acid and other acids (sulphuric, oxalic, and chromic) is small. The pores in the films obtained in these acids can also be completely filled with the electrolytic deposit.[17,124,125] Nevertheless the anodic films formed in phosphoric acid ensure a much greater strength of adhesion of the coatings to aluminium. The structures of sufficiently thick anodic films on different aluminium alloys also differ little,[122] while the strength of the adhesion depends greatly on the type of alloys coated.[9,126]

It has been noted that the electrodeposition of a metal can occur not only in the pores but also on the outer surface of the film[123] as well as on the sharp edges between the hollows in the oxide.[24] These observations led to the creation of the chemical theory of the adhesion of electrochemical metal deposits to anodised aluminium.

2. Chemical theory of the adhesion of electrolytic deposits of metals to anodised aluminium

Aleksandrov, Bogoyavlenskii, and Khudyakov and co-workers[130–137] have developed a chemical theory of the adhesion of coatings to the anodic oxide film. The principal postulates of this theory have been described also in studies by foreign authors.[24,128,129,138] The theory treats the anodic oxide as a colloidal-polymeric formation with semiconducting properties, containing inclusions of anions from the anodisation electrolyte and the components of the aluminium alloys.

According to this theory, the formation of the electrolytic deposit begins simultaneously both in the pores of the oxide and on its surface. The strength of adhesion of the electrolytic deposit to the base is determined not by the mechanical fixation of the deposit within the pores of the oxide layer but by the presence of chemical bonds between the deposited metal and the components of the anodic oxide, mainly the inclusions of anions from the oxidation electrolyte.

The greatest strength of adhesion of the coatings observed when the oxide is formed in phosphoric acid is attributed to the fact that phosphate ions readily penetrate into the anodic oxide during anodisation and create active centres for the electrocrystallisation of metals. The number of crystallisation centres on such oxides is much greater than on oxides obtained in solutions in other acids. It has been observed by the tracer atom method that the number of phosphate ions incorporated in the anodic oxide can be increased by introducing a series of additives (zinc sulphate, polyethyleneimine) or

diminished (sulphuric acid) and hence the strength of adhesion of the coatings to the anodised aluminium can be correspondingly altered.[130,139–141]

The inclusion of the components of the aluminium alloys and their oxidation products in the anodic oxide creates additional crystallisation centres for the deposited metal and hence promotes an increase in the strength of adhesion of the coating to the base. It has been established that the content of the phosphate ions in the oxide increases somewhat with increase in the concentration of the alloy components, which is also accompanied by an increase in the strength of adhesion. Various alloy components promote to different extents the increase in the concentration of phosphate ions in the anodic oxide. These data make it possible to explain, from the standpoint of the chemical theory, also familiar facts such as the difficulties arising in the coating of anodised high-purity aluminium and the dependence of the strength of adhesion on the type of alloy coated.

According to the chemical theory, although the pores in the oxide film do participate in the electrodeposition process they do not play a decisive role. It has been established by X-ray diffraction and electronic spectroscopy[131] that a satisfactory adhesion of the coatings to anodised aluminium can be achieved even when the pores are only slightly filled by the electrolytic deposit. However, the details of the chemical theory have so far been insufficiently worked out to be able to reject the role of pores in the electrocrystallisation processes and in the adhesion of coatings to aluminium oxide.

A positive aspect of the chemical theory is the fact that it creates a basis for the development of a general approach to the analysis of the electrodeposition of metals on oxidised aluminium. The literature of recent years contains data confirming the postulates of both the chemical and the mechanical theory of the adhesion of galvanic coatings to anodised aluminium. It is noteworthy that fundamentally the two theories do not conflict with one another.

3. The development of technological processes for the electrodeposition of metals on oxidised aluminium

Although for reasons indicated, the method involving the deposition of metals on preoxidised aluminium is so far finding limited applications, nevertheless during the last 10–15 years the number of studies devoted to its investigation and improvement has greatly increased. The main bulk of publications were in the USSR, the USA, and Japan. Thus the American Electroplating Society included the study of the electrodeposition of metals on anodised aluminium in its main research projects: Project 41 and Project 61. The results of studies in the USA have been examined by Lashmore,[123,142] Schardein,[122] and Thomas.[143]

Analysis shows that the improvement of the processes for the deposition of coatings on aluminium with preliminary anodisation has the following main aspects: 1) the development of new electrolytes for the deposition of coatings on anodic aluminium oxide and of anodisation procedures; 2) improvement of additional operations for the modification of the anodic oxide and the preliminary preparation of the surface; 3) oxidation and deposition of electrolytic coatings in one bath; 4) combination of the anodisation process with the preliminary liberation of the metal.

Among the current studies devoted to the first aspect, mention should be made of a new technology for the silver plating of anodised aluminium in a highly productive sulphate-ammonia electrolyte,[144] a technology for the nickel plating of anodised aluminium alloys in a sulphate-tartrate electrolyte,[145] a technology for the stepwise anodisation of aluminium articles (reflectors) in a phosphate bath and for the subsequent nickel plating in a citrate electrolyte,[146] and a technology for the copper plating of anodised aluminium alloys.[147] Technological processes for anodisation and subsequent deposition of a series of electrolytic coatings (copper–nickel–chromium, copper–silver, copper–cadmium) on various aluminium alloys have been studied in detail at the Kazan Institute of Aviation and are being introduced into industry.[148–150]

Studies on the partial or complete replacement of phosphoric acid in the anodisation of aluminium by cheaper, mainly sulphuric acid, solutions are being continued. Lukashchuk and Marchenko[151,152] developed a technology for the anodisation of aluminium alloys in a sulphuric acid electrolyte with subsequent electrochemical copper plating. In order to improve the properties of the oxide films, it was suggested that activators—fluorides and fluorosilicates—be introduced into the anodisation solution. These additives increase severalfold the active surface area of the oxide and improve the strength of adhesion to aluminium and its alloys.

The technology for the coating of motor car bumpers made of high-strength aluminium–copper–magnesium alloys with nickel and chromium, developed by Wittrock,[153] has found practical applications in the USA. The first nickel layer is deposited from a sulphamic acid electrolyte on a base anodised in a mixture of phosphoric and sulphuric acids. It was noted that the use of a copper sublayer is undesirable owing to the decrease in the protecting capacity of the coating as a consequence of the enhancement of the contact corrosion in its pores. In one of the latest studies,[126] Wittrock recommends that the anodisation be carried out in a very dilute (3%) solution of phosphoric acid at a high temperature (about 60 °C) with activation of the resulting oxide in sulphamic acid. It is suggested that a sulphamate electrolyte be used for the subsequent nickel plating. The high strength of adhesion of the nickel deposits to the aluminium–zinc–magnesium alloys was noted.

The studies on the second aspect of the modification of the oxide film before the deposition of electrolytic coatings are not fundamentally new. The films are modified in the course of the activation of anodised aluminium—by treatment in dilute acid solutions. The operation became a component of the first technological processes proposed in the 1930's.[3,17] It was established[130] that, after activation, there is an increase in the number of crystallisation centres for the subsequent electrodeposition of the metal, which has a favourable effect on the strength of adhesion of the coating to the base. Best results were noted on treatment of the oxide film in fluoride solutions.

Sulphamic or sulphuric acid solutions have been proposed for the activation of the oxide films.[142,144] It has been noted[154] that the activation of the oxide in sulphamic acid makes it possible to carry out the anodisation process in sulphuric acid and to deposit the electrolytic coatings from electrolytes with the usual composition.

The oxide films can also be activated in the electrolytes for the deposition of electrolytic coatings via a.c. polarisation or by brief electrochemical treatment in solutions for chemical nickel plating.[155,156] In the new technology for the deposition of an iron–nickel alloy on aluminium anodised in phosphoric acid, the activation is carried out in the acid sulphate electrolyte for the deposition of electrolytic coatings.[157] The anodic activation in a dilute solution of hydrofluoric or sulphamic acid after anodisation in a phosphoric acid bath greatly increases the strength of adhesion to aluminium of the nickel coatings obtained in the sulphamate electrolyte.[123]

There have been studies designed to improve the preparatory operations before the deposition of the oxide film. According to Aleksandrov and co-workers,[26,158] etching in 15% hydrochloric acid before anodisation makes it possible to expand the range of permissible phosphoric acid concentrations, the current density, and the process time and also makes it possible to obtain high quality coatings, as regards adhesion, on articles anodised in other acids: sulphuric, chromic, and oxalic. The positive effect of the preliminary etching has been attributed to the increase in the porosity of the oxide films by 5–7%. There is a simultaneous increase in the roughness of the surface, which increases the area of the actual contact between the anodic oxide and the galvanic coating.[141]

The third aspect—anodisation and deposition of galvanic coatings in a single bath—is a comparatively new technological procedure proposed by Mondolfo,[159,160] Bogoyavlenskii and Khudyakov,[161–163] and others. The combination of these two operations is achieved by switching the polarity of the power source. A technology has been developed for the anodisation and deposition of a galvanic coating in a single bath in the preparation of zinc,[164] copper,[160,165–167] cadmium,[165,166] iron,[168] and chromium[169,170] coatings. It was established[164,171] that the nature of the metal cation in the oxidising bath has different effects on the properties of the anodic oxide and the adhesion of the electrolytic deposits obtained from the same electrolyte. The favourable effect of cations is attributed to their incorporation in the oxide film. On deposition of the metal, these cations are reduced, generating additional crystallisation centres and promoting the improvement of the adhesion of the coating to the base.

The advantages of the method involving oxidation and electrodeposition in a single bath consist in the absence of intermediate operations, in which the oxide can undergo undesirable changes, and in a decrease in the total number of operations.[165] However, the operation of a bath in which both oxidation and deposition of the metallic coating take place is fairly complex.

A fundamentally new aspect of the development of the method for the electrodeposition of a metal on oxidised aluminium constitutes the combination of the process involving the preliminary deposition of metals on aluminium films and subsequent anodisation. This aspect is associated with the work of the Japanese investigators Akijama, Yasuchara, and others.[138] It has been established by electron microscopy, X-ray diffraction, and spectroscopic studies that thin films of metals as well as alloy components can be incorporated on anodisation in the oxide film formed in phosphoric acid and can subsequently serve as additional crystallisation centres in the deposition of metals. Japanese workers[138] and subsequently Meckelburg[128] proposed a technology for the copper plating of anodised aluminium involving the preliminary deposition (by a contact or electrolytic process) of iron. On anodisation, the main bulk of the iron coating dissolves but a proportion of it remains as an admixture in the oxide. The preliminary iron plating increases the strength of adhesion of the electrolytic deposits to aluminium and its alloys.

In order to improve the adhesion of the coating the following treatment has been recommended: chemical zinc plating, the removal of the zinc film and anodisation in phosphoric acid, and electrolytic nickel plating.[172] It has been suggested[119] that aluminium can be subjected to an a.c. treatment in a nickel plating electrolyte. A layer of aluminium and nickel oxides is then formed on the surface of aluminium. The current is then changed from a.c. to d.c. and nickel is deposited. It was noted that the metal electrodeposition process can also be carried out in a special bath. In order to improve the adhesion between nickel and aluminium, a final heat treatment of the articles at 100–300 °C is recommended.

An advantage of the above procedure is that it makes it possible to solve the problem of the deposition of galvanic coatings with an oxide sublayer on pure non-alloyed aluminium, while a disadvantage is the increase in the complexity of the technological process.

It is noteworthy that all the proposed improvements have not so far permitted the complete elimination of the main disadvantage of the method—the dependence of the quality of the deposit on the composition of the alloy to be coated.

V. Direct method for the deposition of galvanic coatings

The direct method for the deposition of galvanic coatings on aluminium and its alloys is characterised by the absence of preliminary operations involving the modification of the surface of the base (immersion treatment, anodisation, etc.). The conditions needed to obtain firmly adhering coatings are created directly in the deposition electrolyte by selecting its composition and the electrolysis conditions, while the preliminary preparation of the articles reduces to the cleaning of the surface.

The first attempts at the deposition of electrolytic coatings on aluminium by the direct method refer to the beginning of our century. However, according to Heiman,[87] tests of old patents show that the adhesion of the coatings obtained to the aluminium base does not meet the necessary requirements. Only the direct zinc plating of aluminium in a cyanide electrolyte, proposed by Work,[173] and the Vogt process, quoted after Wernik and Pinner,[3] have found practical applications. Work[173] discovered that, when a cyanide electrolyte is used, it is possible to obtain a satisfactory deposit of zinc on a smooth aluminium surface. In order to improve the quality of the coating, he proposed the replacement of sodium hydroxide in the electrolyte by ammonium hydroxide and the introduction of gelatine as an additive. The subsequent heat treatment of the articles improved the quality of the coating.

The direct zinc plating process in a cyanide electrolyte had been used previously for practical purposes involving the preparation of multilayer coatings.[174] However, the low thermal stability of the resulting coatings and the impossibility of depositing coatings with a thickness greater than 20–30 μm was noted. According to Gruev,[175] heating of the articles above 160–170 °C leads to blistering of the electrolytic deposits.

The Vogt process, developed in 1929 (quoted after Wernik and Pinner[3]), consists of the following main operations: direct electrolytic deposition of a thin layer of zinc from a cyanide electrolyte, brief brass plating in a cyanide bath, and nickel plating in a sulphate electrolyte. In order to strengthen the adhesion of the coating to the base, the articles are subjected to a heat treatment at 230 °C. When necessary, the articles can be additionally chromium-plated. Certain improvements to the Vogt process, concerning the composition of the electrolytes and the electrolysis conditions, were subsequently introduced by Ore[176] and also Edwards and Swanson.[47] Ore[176] recommended that the articles be washed between zinc plating and brass plating and a second heat treatment after chromium plating. The principal change proposed by Edwards and Swanson[47] consists in the additional zincate treatment of aluminium and the removal of contact zinc before the direct electrolytic zinc plating. However, these improvements did not eliminate disadvantages of the Vogt process such as the impossibility of coating alloys with a high

magnesium content (in excess of 3%) and the necessity for the careful maintenance of the recommended treatment conditions.

Among the latest studies on the direct depositions of metals on aluminium, mention should be made of those of Atkinson,[177–179] which provide a preliminary basis for the selection of conditions in the electrodeposition of metals. Atkinson proposed a sulphate nickel plating electrolyte containing fluoroborate ions as the activator and polyligand pyrophosphate–oxalate–amine copper plating electrolytes. However, there is no information about the practical use of these electrolytes.

The principal disadvantage of the methods for the direct electrolytic deposition of metals on aluminium proposed previously, namely the inadequate stability of adhesion of the coatings to the main metal, can apparently be accounted for by the empirical nature and the limiting extent of the studies made.

Since the 1950's, systematic research has been prosecuted at the Ivanovo Institute of Chemical Engineering into the theory and practical application of the direct method for the electrolytic deposition of metals on aluminium.[4] The required electrochemical activity of the surface to be coated was achieved in two ways: by the corrosive interaction of the surface with the electrolyte and by the cathodic activation after switching on the current. Cathodic activation makes it possible to use less corrosive electrolytes and thus reduce the rate of the contact exchange between aluminium and the ions of the metal being deposited. A combination of the two factors indicated above yields stable results as regards the adhesion of galvanic coatings to the base, which are independent of the composition of the aluminium alloy. Under optimum conditions, the strength of adhesion is not inferior to the strength of the main metal.

The present authors' own studies demonstrated the influence of the anionic and cationic compositions of the solutions on the corrosion and cathodic activation of aluminium.[4,180–191] Fluorides are effective activators of aluminium for the deposition on the latter of galvanic coatings. It was recommended that they be introduced into the composition of the electrolytes for this purpose. The characteristics of the influence of these activators on the electrodeposition of metals and the adhesion of coatings as well as the mechanism of their action were investigated over a wide concentration and pH range. The characteristics of the contact exchange between aluminium and the ions of more positive metals present in the electrolyte were studied.

The possibility of the cathodic activation of aluminium in the direct deposition of galvanic coatings had not been established before our investigations, but in a number of instances an increase in the rate of corrosion on cathodic polarisation of the metal was noted. This effect was attributed to a change in the pH of the layer near the cathode as a result of the incorporation of protons in the passive film and its decomposition by hydrogen and also the incorporation of alkali metals into the surface of the aluminium.[192–197]

Our investigations of the cathodic activation of aluminium in the electrocrystallisation of metals[198–201] showed that, in conformity with the ideas of Kabanov and co-workers,[197] Li^+ ions exhibit the most effective catalytic activity.

On the basis of experimental studies on the adhesion of coatings, it was established that it is influenced by electrolytic saturation with hydrogen, as suggested previously. The accumulation of hydrogen at the main metal–coating interface leads to the partial pealing of the coatings in the form of hydrogen blisters. The probability of the formation of blisters increases with increase in current density and depends on the composition of the electrolyte, especially on the presence of hydrogen saturation catalysts or inhibitors. The positive influence of low concentrations of oxidants such as $K_2S_2O_8$ (in the nickel plating electrolyte) and KNO_2 (in the pyrophosphate copper plating electrolyte) has been established.[4,185,202,203] It was also shown for the first time that the introduction into the solutions for the deposition of coatings of small amounts of oxidants can reduce the rate of the contact exchange reaction as a result of the depolarisation of the cathodic corrosion process without appreciable passivation of the main metal.[4,204]

An increase in the adhesion of coatings as a function of time, associated with the escape of adsorbed hydrogen from the main metal–coating interface into the surrounding medium (ageing), has been observed.[205] This process intensifies significantly in the heat treatment of the coated articles, which is frequently used as the final operation in various procedures for the deposition of galvanic coatings on aluminium.

The specific features of the deposition of multilayer coatings on aluminium have been studied. It has been shown that the deposition of upper layers of the coating can lead to a decrease in adhesion and to the formation of blisters as a result of saturation with hydrogen and the corrosion interaction between aluminium and the electrolyte in the pores of the first layer of the coating.[4] The deposition of the upper layer of the coating, for example, cadmium, which can retain hydrogen in the system, can fully suppress the positive influence of the concluding heat treatment on the adhesion of coatings. The conditions and the sequence of the technological operations, which rule out the negative influence of the factors indicated, have been determined on the basis of the studies made.[4,206,207]

Electrolytes for the direct nickel plating, copper plating, and zinc plating have been developed at the Ivanovo Institute of Chemical Engineering and on their basis technological processes for the deposition of single layer and multilayer coatings on various aluminium alloys both in a suspended form and in a loose form in drums have been devised. The technologies thus developed have been included in the USSR Government Standards GOST 9.047-75 and GOST 9.035-84 as well as branch standards and have been applied in industrial undertakings concerned with machine construction, instrument making, and other industries.[4]

In recent years, studies in the field of the direct electrolytic deposition of metals on aluminium have expanded and a considerable proportion of new research has been carried out in the USSR. Attention has been concentrated on the technology of the copper plating and nickel plating of aluminium.

A number of investigations[208–215] were directed towards the further improvement of electrolytes for the coating of aluminium and its alloys, developed at the Ivanovo Institute of Chemical Engineering and also towards their practical application under specific industrial conditions. Thus it has been recommended that sodium sulphate be introduced as a further additive to nickel plating electrolytes;[208] the possibility of replacing sodium chloride by nickel chloride,[209] of sodium persulphate by ammonium persulphate, and of boric acid by sodium acetate[210] has been reported. Data have been published[211–213] concerning the practical use of the electrolyte for the direct nickel plating of articles in a suspended form and in a loose form in drums. It has been suggested that chlorides be used instead of zinc and ammonium sulphates in weakly acid fluoride-containing zinc plating electrolytes.[214,215]

As a result of the study of the properties of polyligand solutions, electrolytes have been developed at the Kharkov Polytechnic Institute for the direct copper plating, bright nickel plating, and

brass plating of cast aluminium alloys.[216–218] A highly productive acid electrolyte based on copper nitrate has been proposed for the direct copper plating of silumin (with subsequent nickel plating and chromium plating).[219]

A patent[220] recommends the use of a pyrophosphate electrolyte for the high speed copper plating of aluminium alloys. The strength of adhesion of the coating to the base is ensured, according to the authors, by the use of a high current density (5–10 A cm^{-2}) in the initial stage of the electrolysis, which leads to the decomposition of the oxide film on aluminium. In a series of reports,[221–224] weakly alkaline electrolytes, containing mixed copper ammine and amine complexes, have been proposed for the copper plating of aluminium articles (especially aluminium sheets). Monoethanolamine, ethylenediamine, pyridine, etc. can be used to prepare the electrolytes. The necessity for the introduction of fluorides into electrolytes in order to improve the adhesion of copper to the base has been pointed out.[223]

Riger[225] suggested a sulphate electrolyte for the direct nickel plating of aluminium and its non-highy alloyed compositions which, together with the traditional chloride and fluoride additives, contains sodium hypophosphite. When this electrolyte is used, high quality coatings up to 40 μm thick, firmly adhering to the base, are obtained. The electrolyte can also be used to deposit wear-resistant composite nickel coatings containing silicon or boron carbide particles. It has been reported[226] that a nickel coating firmly adhering to aluminium is obtained in any electrolyte of the Watts type at a temperature in excess of 150 °C. Kochman et al.[227] recommended a sulphuric acid electrolyte for the direct zinc plating of aluminium, which makes it possible to deposit both bright and black zinc deposits. This electrolyte has found practical use. A complex Niostin electrolyte, based on divalent lead salts and incorporating a reductant and surfactants, has been developed at the Institute of Inorganic Chemistry of the Academy of the Latvian SSR. The application of Niostin ensures the formation of bright coatings on a series of metals, including aluminium alloys.[228]

Technologies have been proposed in which the surface of aluminium is coated by one or two thin layers of metals deposited electrolytically directly on a cleaned surface of the base, after which other coatings are deposited on the surface treated in this way. A technology for the copper plating of aluminium wire, according to which a thin layer (up to 0.1 μm) of tin is deposited electrolytically, before applying the copper coating, from a fluoride electrolyte prepared in a mixed solvent containing ethylene glycol and water has been developed at the Cable Industry Research Institute.[229] It has been recommended[230] that a thin layer of tin be deposited on aluminium articles from an acid fluoroborate electrolyte with subsequent deposition of a bronze (from a pyrophosphate electrolyte) and other coatings from the electrolytes usually employed. In order to increase the strength of adhesion of the coatings to the base, the articles are heat-treated in the concluding stage at 275 °C for 30 min.

A method for the copper plating of aluminium involving the coating of the latter in two stages has been developed in the German Democratic Republic: aluminium is initially coated with a zinc–tin alloy (0.1–0.2 μm) from a fluoroborate electrolyte and then with copper (0.3–0.6 μm) from a pyrophosphate electrolyte at pH 8–8.5. The main copper plating is carried out in a sulphate electrolyte. This procedure is recommended for the copper plating of wire and for the deposition of multilayer protective-decorative coatings.[90] According to the data in Ref. 231, before depositing galvanic coatings the aluminium surface is covered by a layer of iron (up to 1 μm) from a sulphate electrolyte containing fluoroborates or fluorosilicates. After the deposition of the required coatings from the electrolytes usually employed, the articles are heat treated at 150–500 °C. The possibility of using the iron plating electrolytes for the deposition of independent very thick coatings has been noted. Gaynes[232] describes a technology for the iron plating of aluminium alloy with silicon in order to increase their hardness and wear-resistance. This procedure involves the initial electrolytic covering of the base with zinc and then with copper from cyanide electrolytes. Iron plating is carried out in a hot chloride electrolyte. A Hungarian patent recommends that, before depositing a thin layer of nickel from an electrolyte containing fluoroborates, the surface of aluminium should be subjected to additional electrochemical activation in an alkaline solution using non-stationary forms of current.[233]

The development of the direct method for the deposition of electrolytic coatings on aluminium has been stimulated by its simplicity, universality, and the low cost of the technology. At the same time, a considerable proportion of the processes described have been a result of empirical studies. For the development of new highly effective processes, it is desirable to investigate in greatest detail the scientific foundations of the method. There is a prospect of the development of universal electrolytes for the deposition of electrolytic coatings on steel, copper, and aluminium. The use of such electrolytes would make it possible to treat articles made of different materials on a single electroplating line and would ensure greater efficiency of the process.

VI. Other methods

In conclusion we shall consider studies unrelated to the methods listed above. For example, the electrolysis of melts[234] and preliminary deposition of a metal sublayer *in vacuo*[235] or a sublayer of chemical nickel[236] have been proposed for the deposition of coatings on aluminium. It has been recommended[237] that the surface of aluminium be subjected to cathodic activation in hydrochloric acid before depositing a nickel coating. It is suggested that in this case a metastable layer of aluminium hydride is formed on the surface of the specimen. It decomposes during the deposition of nickel, which results in the formation of a strong metal–metal bond. In connection with expansion of the employment of non-aqueous solutions, the corresponding studies devoted to the deposition of galvanic coatings on aluminium have been published.[109,238,239]

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