Modern Methods of Electroplating in the Development of Advanced Coatings

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Abstract: This paper overviews different strategies of electroplating which can be adopted to develop coatings of variety of metals and alloys for better material properties in general, and corrosion resistance in particular. Electroplating technology has grown from the status of an ancient artwork to science, and today into a cost-effective method for production of many materials to meet different applications. Electroplating technology offers a simple and economical route for the synthesis of metal/alloy/composite/multilayer coatings with tailor-made properties. In this context, few strategies of modern methods of electroplating such as composition modulated multilayer (CMM) deposition, magneto-electrodeposition (MED), sono-electrodeposition, composite electrodeposition and sol-enhanced electrodeposition for production of advanced coatings are presented here. A good number of publications on electrolytic synthesis of alloy coatings for various applications, and tuning strategies or post-treatment methods used for enhancing their properties gave a new hope for production of novel materials of better properties using new methods of electroplating as routes. As the global scientific community is looking for a simple and cost-effective material synthesis strategies, in place of expensive and sophisticated techniques, these modern methods of electrodeposition can lead to a new way for the production of coatings with better performances to meet different applications.

Keywords: Electrodeposition; multilayer coating; magneto electrolysis; sono-electrolysis, composite coating.

1. Introduction

Electrodeposition is one of the most reliable and cost-effective techniques for the development of functional materials for various applications. Today, electroplating technology plays a significant role in the synthesis of inorganic materials for various advanced applications in the fields of energy saving [1-4], energy conversion [5-9], energy storage [10-13], and corrosion protection [14-17], etc. Electroplating offers a simple and economical route for the synthesis of metal/ alloy/ metal oxide/ metal hydroxide/ composite/ hybrid systems with tailor-made properties [18-22], having specific morphological features. The process of electroplating allows the production of new materials having unique properties, not attainable by conventional metallurgical methods with great degree of accuracy and reproducibility. Thus, due to incredible claims of electroplating, in terms of their feasibility and potentiality, a large number of research articles are being published annually in the area of material synthesis through electroplating to meet various applications [23-25].

A progressive increase in the number of research papers on electrodeposition and characterization of different metals/alloys has been observed since 2010. Majority of these papers are in the area of energy/ environmental related applications rather than corrosion protective or decorative applications [26-28]]. These evidence the wide acceptance and interest of the whole scientific community in different sectors, like energy, environmental science, materials science, biological sciences etc., without being restricted only to pure science and engineering applications. Many advanced and custom-made electrodeposition strategies using the most modern instruments [29] are emerging out. As a result, today electroplating technology is no more remained as an art of just *dip and deposit,* instead it has grown as multidisciplinary research of industrial applications. In this direction, many modern methods of electrodeposition have come into existence. These

methods basically relied on the principle of modulation in the process of mass transport of cations from the bulk of electrolyte towards cathode surface [30,31]. It is experimented in the development of coatings of many metals/alloys showing better physico-mechanical properties, compared to their conventional counterparts. They may be specified as composition modulated multilayer (CMM) coatings - developed using pulsed cathode current density [32], magneto-electrodeposited (MED) coatings - developed under the simultaneous effect of electric and magnetic field [33], and sono-electrodeposited (SED) coatings – developed under the simultaneous effect of electric field and sonication effect [34]. To this end, the present article presents different methods of electroplating for achieving electroplated coatings of enhanced materials characteristics.

2. Principles of electrodeposition

Electroplating is a technique in which the deposition of metal/alloy/composite coating is obtained through electrochemical reduction of metal ions present in the plating solution [35]. The electrochemistry of plating is governed by Faraday's laws of electrolysis [31,35]. Electroplating needs only simple experimental setup that comprises of an electrolyte commonly known as plating bath, electrodes (anode and cathode) and a direct current (DC) power source. The plating bath is a very important component of the plating technology and it needs to be optimized for the deposition of metal ions from it [35]. The cathode is the substrate on which the coating needs to be developed. Anode is the other electrode that can be the pure metal piece of the metal coating intended to be developed, or it can be an inert electrode such as graphite. The DC power source is the one that drives process of deposition. The properties and performance of electrodeposited coatings can be tuned by proper manipulation of current density. As the electrodes cannot be fixed as anode and cathode, using alternate current (AC) source, it is mandatory to use DC power source to get the deposit on the targeted substrate surface, which is used as cathode.

In electroplating, generally simple salts as the metal source, cheap chemicals as additive and water as the solvent are used. The plating can be achieved on substrate of any size, and any geometry, and in vessels like a simple beaker or in big industrial tanks, depending on the size of the workpiece. As the technique doesn't require any ultra-pure chemicals, costly solvents and sophisticated instrumentation, the technique is very simple and cost-effective [30,35]. The most important one is to optimize the plating conditions, for best performance of electroplated coatings, for the intended use. As the substrate varies, one need to adopt different surface preparation strategies to make the coatings more uniform and adhesive. In galvanostatic electrodeposition, optimization of electroplating conditions (like, composition of the electrolyte, temperature, pH and current density) can be arrived by standard Hull cell method [31, 35]. As the Hull cell method allows the lab-scale optimization to scale up to industrial use, it is the widely accepted method to tune multiple parameters in a single run. The electroplating technique enables the development of metal/alloy/composite coating of desired morphology, thickness, composition (in the case of alloy or composite coatings) etc., by controlling the deposition current density (by keeping the deposition time as constant, for comparison purpose) [30,31,35].

3. Advanced electrodeposition techniques

Electroplating is a good old technique to develop coatings/materials of specific properties by proper modulation of plating conditions. The properties of different metal/alloy/composite coatings can be tailored by proper manipulation of the process of electro-crystallization, during deposition. In conventional electrodeposition, the common strategy adopted to tune the coating characteristics is by adding a proper additive into the electrolyte solution. These additives are believed to get adsorb preferentially at specific crystallographic planes, and thereby change the growth mechanism [31]. However, coatings with enhanced materials characteristics can also be developed by bringing variations on the mass transfer process at the electrode/electrolyte interface during deposition. In this regard, development of multilayer coatings [32, 36-40], magnetoelectrolysis [33,41-44] and sonoelectrolysis [34,45,46] are promising techniques to synthesize new materials with advanced characteristics by bringing periodic modulation in

mass transport process at the cathode, during deposition. Apart from these, composite electrodeposition [47,48] and sol-enhanced electrodeposition [49-51] techniques are also attaining much attention as simple and reliable strategies for the development of composite coatings with tailor-made properties, suitable for various advanced functional applications. A general discussion on modern plating techniques is presented here just to illustrate how electroplating technology can be used as a definite tool of indefinite possibility in the development of new materials of better corrosion protection and electrocatalytic activities of alkaline water splitting.

3.1 Composition modulated multilayer coatings

The corrosion protection efficacy of conventional monolayer metal/alloy coatings can be improved to many folds of its magnitude by composition modulated multilayer (CMM) or simply multilayer techniques. CMM coatings consist of a sequence of two metals/alloys, alternately deposited one above the other (Fig. 1), achieved by modulating the structure and composition of each layer through precise control of deposition current densities. As the composition and structure of the developed coating greatly depend on the deposition current density, multilayer coating can be achieved by bringing a periodic variation in deposition current densities, which can give different structure and composition of alternate layers [36-38]. Then, on cycling the selected deposition current densities, for a fixed deposition time, multilayer alloy coatings with different number of layers can be developed. As the coating formed at one current density is different from that in other (in both composition and structure), a laminar coating having alternatively different composition, called multilayer coatings are formed [32]. Cross-sectional view of monolayer, and multilayer coatings with different degree of layering on the surface of substrate is shown in Fig. 1.

Generally, nano-layered coatings (when thickness of individual layers are reduced to nano-meter scale) resulted with the formation of several new interfaces between layers, and is shown in Figures 1(a) and 1(b). The enhanced corrosion protection efficacy of multi-layer coating compared to the conventional (monolayer) alloy coating is attributed to the formation of new interfaces. Due to the presence of many interfaces, corroding medium spreads laterally through those interfaces (between two nano-layers), and thereby prevents direct penetration of the corroding medium into the substrate [36]. Thus, the presence of multilayers is responsible for the delayed spreading of corrosion towards the substrate is shown schematically in Fig. 1. However, in the case of conventional alloy coating, the corroding medium penetrates directly into the substrate, *i.e.*, the time required for the corroding medium to penetrate through the coating, and to attack the substrate in multilayer coating (T_1) will be greater than the time required in conventional alloy coating (T_2). Hence, the protection efficacy of multi-layered coating is significantly greater than the conventional alloy coating. However, the effectiveness of multi-layer coating largely depends on the composition, thickness of individual layers, and total number of layers in the coatings.

3.2 Magentoelectrolysis

Magneto-electrolysis or magneto-electrodeposition refers to the process of electrodeposition in the presence of induced magnetic field. As the plating process works by combining the effects of both magnetic field and electrolysis, it is termed as magneto-electrolysis, or simply magnetolysis. It is well

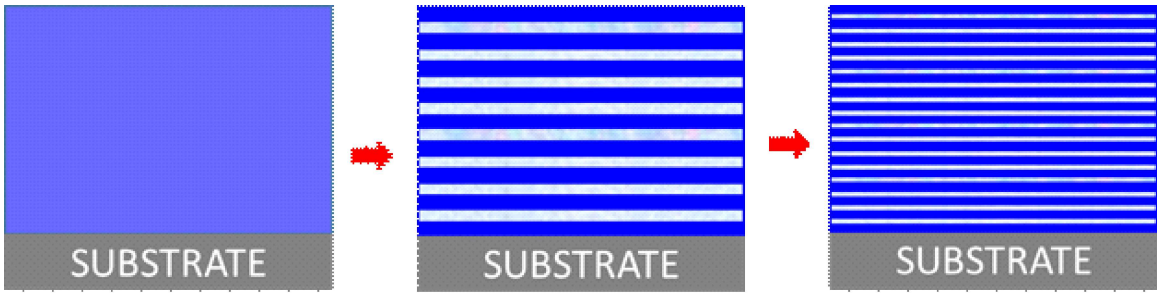


Fig. 1. Cross-sectional view of monolayer, and multilayer coatings with different degree of layering on the surface of substrate

know that the superimposition of magnetic field *(B)* on the process of electrochemical reactions has significant effect, which comes under the topic called, magneto-electrochemistry. It is inherently an interdisciplinary subject including concepts of magnetism, hydrodynamics and electrochemistry [52-55]. The results of magneto-electrochemistry are unique, and sometimes surprising, and they seldom take us to unexpected insights of fundamental process of electrochemistry having new practical applications. Magneto-electrochemistry, or in short magnetolysis encompass four major aspects of electric-magnetic field interactions. They are: *i)* magnetic field effect on electrolyte properties, called magneto-hydrodynamic (MHD) effect, *ii)* electrolytic mass transport, driven by applied current, *iii)* to small extent on electrode kinetics, and *iv)* nature of electrodeposit [33, 54-56]. The well know MHD effect generally speaks about the effect of applied *B* on electrochemical processes, and is governed by famous Lorentz force. [52, 54]. Hence, the applied magnetic field can bring change in mass transfer at the electrode/electrolyte interface (Fig. 2).

The superimposition of an external *B* can bring changes in the electrolyte in terms of flow patterns, extent of mixing and current density distribution, and thereby results in a significant variation in the rate of deposition process. The deposit characteristics like nucleation, growth, texture, phase composition, hardness, preferred orientation, morphology, etc. are reported to be greatly influenced by the presence of an external magnetic field during deposition [33,41, 44,56]. However, the effect of applied *B* on the electrodeposition process and the characteristics of the developed coating is greatly influenced by other factors such as the intensity and direction (parallel or perpendicular with respect to the direction of applied current) of the induced *B*. As the MHD effect, arises mainly due to Lorentz force, is responsible for bringing out all the changes in mass transfer or forced convection during MED, the maximum influence of applied *B* on deposition process is expected to happen when the extent of Lorentz force ($F_L = qvB$ sinθ) is maximum [33,56]. Hence, the maximum influence of *B* on MED process can result when *B* is applied in perpendicular direction (θ=90°) to obtain maximum MHD effect induced by Lorentz force [33,41].

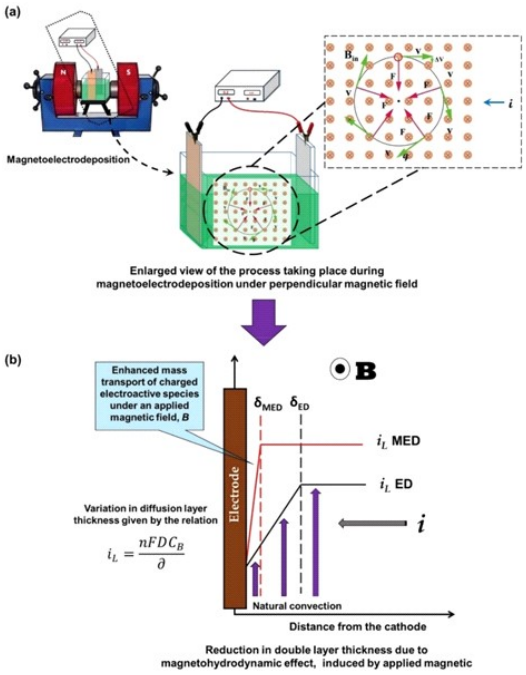


Fig. 2. Representative diagram showing the process of magneto-electrodeposition under induced magnetic field, applied in perpendicular direction: a) the migration of cations, and b) enhanced mass transport influenced by the reduction in double layer thickness [after ref. 33].

Apart from the effect of applied *B* on the electrodeposition process, it can also bring changes in electrocatalytic water splitting reaction, another electrochemical process widely used for the generation of hydrogen. The enhanced mass transfer due to MHD effect in the presence of an external applied *B* during electrocatalytic water splitting reaction is reported to be beneficial in reducing the polarization resistance as well as the ohmic drop due to bubble resistance [57-59]. In magneto-electrolysis, superimposition of perpendicular magnetic field *B* enable the easy detachment of gas bubbles from the electrode surface by reducing the over potential arising from polarisation and bubble resistance [57]. It may be attributed to the MHD effect, which is maximum when applied *B* is perpendicular to the direction of movement of ions, explained by Lorentz force ($F = q \times v \times B$ Sinθ).

3.3 Sonoelectrolysis

The effect of superimposition of ultrasound on the process of electrolysis is beneficially utilised in the sono-assisted electroplating called as

sonoelectrolysis. Generally, when ultrasound effect is induced to a liquid media, a variety of processes do take place, leading to unusual physical and chemical changes in it. These include cavity effect and implosion of liquid at near electrode surface [34, 45]. In the case electroplating, the induced ultrasound effect provides an increased mass transport by forced convection, which eventually truncated, or thinning the Nernst diffusion layer. The acoustic energy generated in the plating medium, due to the induced ultrasound effect is mechanical in nature. When ultrasound effect is superimposed through homogeneous conducting medium, all molecules will be set to vibrate, and making them to stretch and compress alternatively [34]. Consequently, spatial distances between molecules will change as molecules are set to oscillate about their mean position. As the power density of applied ultrasound effect is increased to stage, where intramolecular forces are not in a position to hold the molecular structure intact. At this point of time, implosion takes place where cavitation bubbles are created [34, 46]. Thus, the created motion of ions through forced convection, due to cavitation force leads to the enhanced transfer of ions towards cathode surface, and thereby results in the development of coatings, having different compositional and morphological changes.

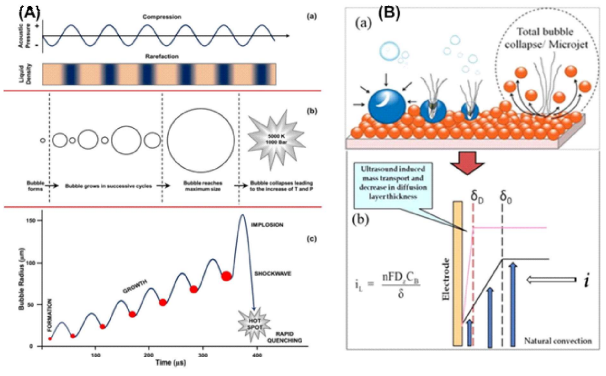


Fig. 3. Schematic diagram showing on left: (A) effect of power ultrasound in liquid medium; a) acoustic compression, b) implosion of bubble at its maximum size, after its steady process of contraction and expansion, and c) formation of 'hot spot' after sudden quenching; and on right (B) illustrating the effect of ultrasound at electrode-electrolyte interface leading to: a) acoustic cavitation collapse, and b) decrease in the diffusion layer thickness due to effect of ultrasound [after ref. 34].

Therefore, sono-electrodeposited coatings having different crystallographic orientation will exhibit different properties, than their conventional coatings. The extent of influence of the applied ultrasound on the plating process is greatly influenced by the power density and direction (with respect to the direct of the deposition current) of the applied ultrasound field. Further, sonoelectrolysis can be effectively utilised for the development of multilayer coating by controlling the ultrasound effect to go 'ON' and 'OFF' alternatively, parallel to the process of constant current electrodeposition. The periodic modulation in power density, achieved by tuning the sonicator probe to go 'ON' and 'OFF' can bring periodic modulation in mass transfer process, to form the coating in multilayers [46].

3.4 Composite electrodeposition

Composite coatings is of great importance due to its possibility to develop new materials of specific properties to meet many practical applications. The extensive research work progressed in the area of composite coating lead to the development more advanced materials, with equal provision to tailor their properties. In this regard, electroplating is the most practically viable approach for developing high performance composite coatings by proper manipulation of plating conditions, and by using variety of nanoparticles. The properties of composite coatings can be varied by varying the size of dispersed particles (micro/nano), compared to that in other techniques like powder metallurgy, vacuum deposition and metal spraying [16,47]. The composite electrodeposition is essentially a co-electrodeposition of ceramics, metal-based particulates, fibres etc. (which are basically insoluble inorganic particles), dispersed in the plating bath with metal ions. Number of publications are available in the literature on metal/alloy matrix composite coatings, highlighting their production and applications. The process of co-deposition, in other words inclusion of nanoparticles into the coating matrix is determined by particle characteristics (like its shape, size, concentration, surface charge etc), chemistry of electrolyte (its concentration, temperature, pH and additives), current density and mass transfer process involved [47,48]. Hence, the effective development of metal matrix composites can be achieved by tuning the plating bath and deposition

conditions effectively by close control over the deposition current density. The mechanism of composite electrodeposition and the steps involved in the incorporation of nanoparticles into the metal/alloy matrix is schematically represented in Fig. 4.

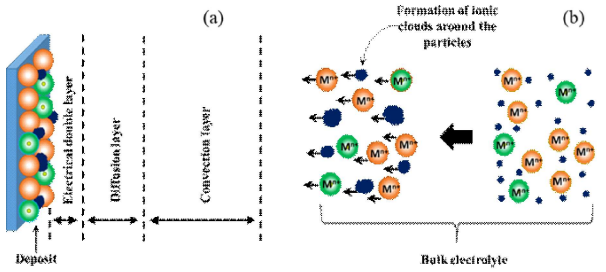


Fig. 4. Diagrammatic representation showing: (a) Electrode-electrolyte interface during co-electrodeposition, and b) process of co-electrodeposition from electrolytic bath having metal ions and nanoparticles [after ref. 48].

3.4.1 Sol-assisted electrodeposition

The most important limitation of composite coating using solid nanoparticles can easily be resolved by having the homogeneous dispersion of colloidal particles in the bath. This process is called sol-assisted electrodeposition. If particles are superfine/nano in nature than micro size, then incorporation of second-phase particles (inclusions) is found to be very effective to impart better properties to composite coatings. The nano-sized particles obviously give high dispersion, which lead to strong interaction of particles with metal/alloy matrix. In composite electrodeposition, good dispersion of the nanoparticles can be properly maintained by following different methods, like vigorous agitation, air injection, ultra-sonication, by adding surfactants [60]. But, due to very large specific surface area of nanoparticles, it is very difficult to achieve a homogeneous solution of electrolytic bath, without having the agglomeration of nanoparticles. In this direction, sol-assisted electrodeposition is an elegant approach to develop composite coatings, with homogeneously dispersed nanomaterials. Thus, sol-assisted electrodeposition method encashes benefits both sol-gel process and composite electrodeposition [49-51]. The sol-enhanced composite electrodeposition can be accomplished by adding a small amount of in-situ liquid-phase synthesized nanoparticles into the electrolytic bath of metal/alloy. This method enables the in-situ formed nanoparticles to integrate immediately into the metal/alloy deposit, alongside the deposition of metal ions to form compact nanocomposite coating [49]. Thus, sol-assisted electrodeposition method avoids the natural agglomeration of nanoparticles. There are reports on sol-assisted electrodeposition of TiO_2 for development of homogeneous composite coatings to meet many applications [50-51].

4. Concluding remarks and perspectives

As electroplating technology has grown from the status of artwork in the ancient period of its origin to a cost-effective engineering technique at present, plating has been attracted as a reliable technology for the development of functional materials for various applications. The current research trend clearly indicates that electrodeposition plays a significant role in the synthesis of materials for various advanced functional applications in the fields of protective coatings and energy saving, energy conversion, energy storage etc. Hence, the recent publications on material synthesis through electrodeposition imply that good old deposition technique still attains much attention, and its technology is getting modified from time to time with the advent of modern power sources to meet the requirements of advanced applications in the emerging fields. A large number of publications on electrolytic synthesis of various functional materials for different applications, and different tuning strategies or post-treatment methods used for enhancing the material characteristics of electrodeposited materials gives a new hope for the production of new materials of better properties, using different methods of electroplating as routes. As the global scientific community is looking for a simple and cost-effective material synthesis strategies in place of cost-effective, and sophisticated techniques, the effective utilisation of modern electrodeposition techniques can boost simple and straight forward method of material synthesis to meet various applications, in the near future.

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