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Electrodeposition of laminar coatings of Ni–W alloy and their corrosion behaviour

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ABSTRACT

The attractiveness of electroplating for the synthesis of advanced materials is linked to large selection of plating conditions coupled with different mass transfer processes towards the cathode, and this allows the tailoring of different properties of many electrodeposited coatings. This theme has been exploited effectively in the development of a new class of coatings; called composition modulated multilayered (CMM), or in short laminar coatings. The work embodied in this paper is to demonstrate how the corrosion resistance of monolayer Ni–W alloys can be increased to many fold of its magnitude by multilayer deposition. Ni–W coatings have been deposited on mild steel (MS) in a laminar multilayer pattern from a citrate bath using single bath technique (SBT). Electrodeposits having alternate layers of alloys, having different compositions were developed by modulating the direct current (DC). CMM coating configurations have been optimized from a newly developed bath, in terms of current pulse height and thickness of each layer to maximize its corrosion protection ability, in relation to its monolayer coating, developed from same bath for same time. The process and product of the Ni–W coatings have been characterized using different instrumental methods, such as cyclic voltammetry (CV), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) study. The better corrosion resistance behaviour of CMM Ni–W coatings has been analysed in the light of increased surface areas of the coatings due to layering, and results are discussed.

1. Introduction

Recently electrodeposition of Ni-based alloys with transition metals, such as tungsten (W) or molybdenum (Mo) has taken importance due to their enhanced surface performance properties. Among them Ni–W alloy coatings are of considerable interest due to their wide range of engineering applications [1]. Apart from good mechanical, tribological and magnetic properties, the electrodeposited Ni–W coatings offer excellent corrosion resistance and electrocatalytic characters [1,2]. It has been reported that Ni–W alloy coatings can be an important alternative for hard chromium coatings [2] as it has to be eliminated from the manufacturing processes, e.g. in the aviation and automotive industries, due to environmentally hazardous hexavalent chromium [1,3].

It is well known that elements like W, Mo, Ge, P etc. cannot be deposited directly from their aqueous solutions. However, they may readily be codeposited with Fe-group elements like Fe, Co and Ni. In this connection the term *induced codeposition* was coined by Brenner in 1963 [4], to describe a situation where, 'a metal that cannot be deposited alone from its aqueous solution can be codeposited in the presence of another metal, forming an alloy' [5]. Of late, Sridhar et al. have done an extensive literature review on electrodeposition of Ni–W alloys and studied the effect of Ni^{+2}, Cit^{+3}, additives, applied current density (c.d.) and bath temperature on the Faradaic efficiency, W content, and properties of Ni–W alloys deposited on stationary working electrodes [4]. It described the induced type of codeposition taking place during electroless deposition of Ni–P alloys alongside the deposition of alloys of W and Mo with the Fe-group metals. Actually several hypotheses have been advanced to explain the mechanism of the induced codeposition. Among them, the most favoured hypothesis is ennobling of the deposition potential of W by virtue of the formation of a solid solution or inter-metallic compound [6]. According to which the codeposition of W is based on the assumption that the deposition potential of W is too negative (-0.51 V) to be attained in aqueous solution. It was assumed that the formation of a solid solution of W with the Fe-group metal involves a sufficient decrease of free energy to shift the deposition potential of W to more positive (more noble) potentials. This hypothesis is considered to be more acceptable, and referred to as the shift of the deposition potential. Tsyntsaru et al. [2] also recently presented an overview of the research dealing with electrodeposition of W alloys with Fe-group metals, describing the chemistry of electrolytes, codeposition mechanisms, physicochemical properties and applications of W alloys as a main alternative to sustain the hard chromium coatings.

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Today in surface coating technology research as a part to achieve better corrosion protection, the focus has been given for development of laminar (multilayer) coatings instead of their monolayer (monolithic/homogeneous) coatings. In this direction, several studies have been reported to support the fact that periodic modulation in the mass transport process at the cathode, i.e., by altering the c.d. during deposition allows the growth of coating with periodic change in composition [1,5,7]. Such type of coatings having laminar structure of alternate composition is called composition modulated multilayer (CMM) coatings. If multilayer coatings are developed from a bath having ions of two metals, i.e., from alloy bath by proper modulation of the c.d. (periodically), then the coatings are called composition modulated multilayer alloy (CMMA) coatings [8]. The CMMA coatings exhibit better mechanical strength, wear, elasticity, ductility, electrical, optical and corrosion properties, compared to their monolayer coatings. The improved properties of CMMA coatings are attributed to the increased effect of surface or interface arising from the exceptional thinness of the layers [8,9]. Hence properties of CMMA coatings observed to be increased with increase in number of such layers. Hence owing to their unique technological properties, the CMMA coatings exhibit a wide range of applications different from pure metals and homogenous alloys. Single bath techniques (SBT) and dual bath techniques (DBT) are the two methods for producing electrodeposited CMMA coatings. In SBT, the metal ions required to form alloy of two or more composition are dissolved in a single electrolyte and cathode potential is made to change alternatively. To avoid their simultaneous deposition, a large potential difference must exist between the deposition potential of metals. The dual bath technique involves the deposition of alloys of alternatively changing composition from two separate baths. Both techniques have their own advantages and disadvantages, however the drawbacks of the DBT have been deemed to outweigh the benefits, so that the SBT approach is commonly used [10].

Many researchers have already reported the development of high corrosion resistant Ni–W alloy coatings by electrolytic method from different baths explaining the induced type of codeposition followed; and dependency of deposit characters with bath composition and operating parameters. Lee et al. [7] recently reported the mechanical properties of electrodeposited Ni–W alloy multilayers, using SBT. But to the best of author's knowledge, no work is reported in relation to development CMMA coatings of Ni–W alloy by SBT. Hence, in pursuit of developing good corrosion resistant coatings, a new Ni–W alloy bath has been proposed for development of monolayer Ni–W alloy coatings using direct current (DC). The corrosion resistance characters were then increased by developing laminar coatings using pulsed DC. The main focus of this work is to optimize coating configuration of multilayer Ni–W alloy coating, in terms of number of layers and height of pulsing DC. A new bath formulation with operating parameters has been optimized, and mechanisms of codeposition with/without additives were studied using cyclic voltammetry. The effects of current pulse, in terms of duration and height, on the composition of individual layers, and formation of layers during coating have been studied. Advanced instrumental techniques such as scanning electron microscopy (SEM), Energy Dispersive X-ray Analysis (EDS) and X-ray diffraction (XRD) study have been used, to support the reasons given to explain the improved corrosion resistance of multilayer coatings of Ni–W alloy.

2. Experimental

2.1. Optimization of Ni–W bath

Monolayer Ni–W alloy coatings were electroplated on MS from aqueous solution having $NiSO_4 \cdot 6H_2O$ (Nickel sulphate hexahydrate), $Na_2WO_4 \cdot 2H_2O$ (dihydrated sodium tungstate) and $C_6H_5Na_3O_7 \cdot 2H_2O$ (tri-sodium citrate dihydrate), used as complexing agents. To regulate the plating process other parameters like pH and conductivity, H_3BO_3 (boric acid) and NH_4Cl (Ammonium chloride) were used as buffer and conducting salts, respectively. The glycerol was used as an additive to increase the brightness of coatings. All reagents were prepared in deionized water; and plating was carried out under alkaline condition (pH = 8.5). H_2SO_4 and NH_4OH were used suitably to fine-tune the pH of bath. The ammonium salt in the plating bath is assumed to increase solubility of the compounds of the metals and thus stabilizes the bath against gradual precipitation of metal tungstates, and to increase the Faradaic efficiency (FE) of alloy deposition by depressing the H_2 evolution. Generally in tungstate bath, nickel is found to exist partly as an ammonia complex and partly as a complex with citrate ion as observed by Brenner and his co-workers [5]. Conventional Hull method was used to optimize the bath composition and operating parameters as described elsewhere [10,11], and is given in Table 1.

2.2. Experimental procedure

All depositions were carried out in PVC cell of 200 mL in capacity using DC Power Analyzer (Agilent N6705A, USA). The MS plates of 2.5 × 2.5 cm^2 surface area were exposed to plating solution after metallurgical polishing, followed by degreasing with trichloroethylene (TCE) and then by alkali cleaning. Just before immersing in the bath, the plates were activated by pickling in 10% HCl. Graphite plate, having the same active surface area was used as an anode, in compliance with the practise of using insoluble anodes in ammoniacal baths introduced by Brenner A [5]. All depositions (both monolayer and multilayer) were carried out galvanostatically for 10 min at constant temperature (303 K). All deposition conditions except current density (c.d.) were kept constant. The monolayer Ni–W alloy coatings were deposited by passing DC at required current density. Driven by the fact that periodic modulation in mass transport process at cathode film (by periodic change in the current density) leads to the development of multilayer coatings (with periodic modulation in composition) on the surface of cathode, CMMA Ni–W coatings were developed. The power pattern used for deposition of monolayer and multilayer alloy coatings, and their corresponding coatings developed are shown schematically in Fig. 1. Conveniently, CMMA Ni–W coating having alternatively different compositions was represented as: $(\text{Ni–W})_{1/2/n}$. Here 1 and 2 indicate the first and second cathode current densities which are selected to be applied for deposition of alloys of different composition and 'n' represents the number of layers formed during total plating time, i.e., 10 min. Hence, CMMA Ni–W coatings with different coating configuration, i.e., under different sets of CCCD's and with different number of layers were developed, and are subjected to characterization. By proper setting-up of the power source, the cyclic cathode current densities (CCCD's) were set to change alternatively, during deposition of multilayer coatings. The coated surfaces were rinsed with distilled water several times, dried in hot air and desiccated under vacuum till further analysis [10].

Table 1
Composition and operating parameters of optimal bath for electrodeposition of bright Ni–W alloy.

Bath composition	Concentration (M)	Operating parameters
Nickel sulphate hexahydrate ($NiSO_4 \cdot 6H_2O$)	0.09	pH : 8.5
Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$)	0.14	Temperature : 303 K
tri-Sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$)	0.35	Anode : graphite
Boric acid (H_3BO_3)	0.32	Current density range: 1.0 A dm^{-2}–4.0 A dm^{-2}
Ammonium chloride (NH_4Cl)	0.67	
Glycerol ($C_3H_8O_3$)	0.12	