CHAPTER 1

INTRODUCTION

1.1 Short fall of hexavalent chromium

Conventionally adopted chromium baths (Cr-VI) are becoming obsolete due to the increasing health and environmental awareness and more of alternatives are in practice. Hexavalent chrome has been extensively used in applications in the aerospace, agriculture, fastener, metal manufacturing and oil service industries. Hard chromium is the best known electrodeposit for engineering/ functional applications. Despite their excellent functional properties there is an increasing drive to find a replacement for hard chrome due to environmental concerns of using hexavalent chromium containing sulfate or fluoride as catalysts during the plating process. For the same reason, EPA/OSHA regulations have placed severe restrictions on the hexavalent chromium plating process. According to the work safety and hygiene regulations, expensive breathing apparatus for the employers, pricey exhaust systems for vapor purification in the workshops and, in particular, effluent treatment is very complex, which requires special disposal methods.\(^1\) Hexavalent chromium in solution is also a recognized carcinogen and causes other health problems such as skin and lung irritation.\(^2\) Furthermore, Cr coatings are known to deteriorate in hardness and corrosion resistance under operating temperatures higher than 205°C due to the thermal motion of atoms that weakens the bonding strength.\(^3\)\(^-\)\(^5\)
Difficulty in maintaining the uniformity of coating thickness during plating and in practical it has the efficiency of $\sim 15\%$. In view of this, electroplating of hexavalent chromium has been restricted from the industry in U.S, European Union, China, Japan and it is going to face possible extinction throughout the world in the near future. This problem spurred the researchers to develop an alternative to hexavalent chromium plating, which has become an important goal of modern electrochemistry. The investigation of literature on the alternatives for hexavalent chromium plating suggests that Ni-W, Ni-P, Co-W, trivalent chromium and ternary or quaternary alloys, functionally graded deposits were considered as potential alternatives to replace Cr(VI) plating process. Several researchers claimed that trivalent chromium is going to be one of the best substituents to replace hexavalent chromium. Nevertheless, up to date, trivalent chromium is restricted to decorative appliance, due to their inability to deposit thick coatings with acceptable quality. Those alloys still underperform hexavalent chromium in many factors. Tungsten, as it belongs to the same group (VI) with similar chemical and electrochemical properties, it is considered as one of the alternatives to the hexavalent chromium metal. Ni–W is nominated as a promising environment-friendly alloy for replacing hard chromium due to the suitable appearance of the coating and its mechanical and anti-corrosion properties. Furthermore, the toxicity towards the aquatic species is low, and the industrial production of these coatings will produce environmentally harmless wastewater.

1.2 Influence of acidic solutions

Corrosion is a process of material deterioration or surface damage in an aggressive medium. Pure metals and alloys react chemically/electrochemically with corrosive medium to form a stable
compound, in which the loss of metal occurs. The compound so formed is called corrosion product and metal surface becomes corroded. Corrosion involves the movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an acceptor at less active areas (cathode), an ionic current in the solution and an electronic current in the metal.\textsuperscript{10} The protection of metals from corrosion is always a hot topic to be dealt with, which aids in increasing the lifetime of metal and resulting in huge savings.\textsuperscript{11} An important attribute of any structural material is its resistance to corrosion.\textsuperscript{12} Surface is the most important part of any engineering component. It is well known that most components fail from surface initiated defects such as wear, corrosion, fatigue or fracture.\textsuperscript{13} Mild steels are one of the leading engineering materials over years for many scientific and industrial applications, especially in automobile and aero-system industries, because of their unique properties.\textsuperscript{14} It is one of the least expensive steels exhibiting the favorable properties such as high hardness, easy weldability, and good durability, which allow for the passage of electric current throughout the metal without distortion.\textsuperscript{15} Yet, their susceptibility to corrosion attack, poor tribological resistance limit their applications in industry and in engineering components.

Acidic solutions are widely used in the industries due to the applicability in the chemical cleaning of scale in metallurgy, oil recovery, petrochemical industry and in the acid pickling of iron and steel.\textsuperscript{16} During this acidic application, in particular with the use of hydrochloric and sulphuric acid the corrosion of metal is extreme.\textsuperscript{17} Moreover, the sulphate ion is more aggressive than the chloride ion in neutral and alkaline medium solutions provoking pitting.\textsuperscript{18} Localized corrosion is one of the fatal drawback for the industrial application of electrodeposited metal films that deteriorates the anti-corrosion ability, caused by the presence of cracks.\textsuperscript{19-20} Majority of industries are inherently faced with the problem of corrosion. Production of robust
oxidation and corrosion resistant coatings are the most important requirement by the industry, which can increase the service life of the materials even under severe environmental conditions.\textsuperscript{21}

1.3 Impact of Ni-W as a substitute to hexavalent chromium

Electrodeposited nickel has been used to give the decorative and functionally suitable metal coatings for various applications such as electroforming of printing plates; photographs record stumpers, foils, tubes, screens, service apparatus, automobiles, and aviation. Nickel coatings can significantly improve mechanical, tribological, anticorrosion, magnetic and magneto transport properties. It is well known that nickel plating from sulfate–chloride Watts type bath has been commercialized. Nonetheless, nanostructured nickel is generally unstable, which may lead to a rapid grain growth even at low temperatures.\textsuperscript{22} One of the reason is its low melting point (1455°C) which lacks its thermal stability. It is anticipated that the thermal stability of nickel can be improved if the melting point of the coating is increased. Alloying with some metals of high melting points has been found to improve stability of that system.\textsuperscript{23}

Amongst the various metals, tungsten has the highest melting point (3422°C) that could improve thermal stability and maintain the nanocrystalline structure at a wider temperature range. Tungsten and its alloys founders wide applicability as surface coatings, to protect the metals from corrosion. The interest in the electrodeposition of Ni-W alloys has been raised due to their unique combination of mechanical (high tensile strength and hardness), tribological (wear resistance), thermal (high melting point, hot strength, oxidation resistance), electrocatalytic (hydrogen evolution), magnetic, and electrical properties. Tungsten alone cannot be electrodeposited from the aqueous solution, because of the evolution of hydrogen gas prior to reaching the
required reduction potential. Review of literature by Holt and Kahlenberg, suggest that thin films of pure tungsten could be electrodeposited by electrolyzing different alkaline baths. Nevertheless, this was proved incorrect by the same, because of the appearance of metallic iron in the electrodeposits as impuri. The electrodeposition of pure tungsten and molybdenum coatings from tungstate solutions is hindered by the formation of an oxide layer because of hindrance for the reduction to the metallic tungsten directly due to a low overvoltage for hydrogen evolution on tungsten. Hence, a further reduction to metallic tungsten does not proceed, and the entire current is consumed for hydrogen evolution. On the contrary, tungsten and molybdenum ions do co-deposit with iron group metals so that alloys containing a high content of refractory elements are obtained. However, the electrodeposition of Ni–W alloys is made possible with the help of induced co-deposition process. Brenner was the first one to electrodeposit Ni–W alloys from alkaline sodium citrate bath. Using the same plating bath in 1998, Yamasaki has advanced its size to nano crystalline range that has opened up new possibilities in the usage of Ni–W alloys. Their unique combinatorial properties of tribological, magnetic, electrical, good corrosion resistance, and wear resistance, permit their use in the magnetic recording of information, magnetically controlled relays, resistors, axletree, cylinder, and high-temperature glassy mold and electrodes of hydrogen energetics. Its unique combinatorial properties ascribe to the W phase in the alloy system that possesses superior intrinsic hardening effect and corrosion resistant properties. Its high bending ductility and intense hardness, makes the usage of this alloys in molding process, for LIGA (a German acronym for lithography, electroplating and forming) applications. T. Yamasaki reported that Ni-W alloy containing tungsten of about 20.7 at. % with an average grain size of about 3 nm has been obtained with the tensile strength of about 2300 MPa. Likewise, its uncomplicated fabrication process, low-cost and efficient electrocatalysts, makes its usage as crucial, in fuel cell electrodes, which is one
of the major defies in fuel cell electrocatalysis.\textsuperscript{33} Their high temperature corrosive resistant property appealed them to use as a functionally gradient material (FGM) a new kind of engineering material, which was first introduced as a thermal barrier material for spacecraft and further in medical, electronic and nuclear energy industries with a minute change in its composition and structure.\textsuperscript{34} Some of the notable applications that contributes for its high temperature resistance are turbine blades,\textsuperscript{35} manufacture of injection nozzles in combustion engines\textsuperscript{36} and as a substrate for high temperature superconductor\textsuperscript{37}. In addition, its high hardness (\textasciitilde 7 GPa)\textsuperscript{38} expands its applicability in several engineering industries, as compared to \textasciitilde 2 GPa for Ni metal deposited from the conventional Watt's bath.\textsuperscript{39} It has been reported that electroplated Ni–W alloys with amorphous/nanocrystalline structures can be used in the molding process of microfabrication system using the lithographic galvanic deposition technique (LIGA).\textsuperscript{40} Moreover, its robust corrosion resistance property, i.e. corrosion rate of Ni-W film in HCl solution at 30\textdegree C was only 1/40 of 304 stainless steel\textsuperscript{41} that anticipates its use in as the barrier between copper and silicon in the next generation of ultra large scale integration circuits (ULSI) and micro electromechanical systems (MEMS).\textsuperscript{42} Furthermore, electrodeposited Ni–W alloys show good properties for the oxygen reduction reaction (ORR) in oxygenated unstirred 1\% sodium hydroxide solution, suggesting possible applications for the acceleration of the hydrogen evolution from alkaline solutions.\textsuperscript{43}

1.4 Significance of Electrodeposition

Many techniques have been proposed for the fabrication of Ni-W alloys. Some of them are physical and chemical vapor deposition, thermal spray, magnetron sputtering, electrodeposition, thermal spray and vacuum-based techniques such as sputtering and molecular beam epitaxy. Despite development of new technologies, traditional electroplating still plays an important role in surface enhancement\textsuperscript{44} and it is considered as an intrinsically
Advantages of electrodeposition over other synthetic methods (e.g. electrospinning or lithographic procedures) include: ease of operation and time-effectiveness, strict control of the wire length, precise tuning of the chemical composition and microstructure (i.e., crystallinity), and possibility to produce multilayered wires consisting of different segments with dissimilar compositions along the wire. Key note features of this technique, (a) allows to coat large substrates even when they have complex geometries by tuning conditions for conformal growth, (b) desired change in the size of alloy deposits of nano/microstructured coatings with different surface properties, with a simple change in the processing parameters (ex. current density, temperature, time, pH or plating bath composition), (c) porosity-free deposits that do not require subsequent consolidation processing, (d) low energy requirements, (e) rapid deposition rates, (f) time-effectiveness (g) simple scale-up with easily maintained equipment and so on. Therefore, Electrodeposition is a technologically feasible and inexpensive method to fabricate strong and relatively ductile metallic materials in bulk form or as coatings. D.G. Morris reported that electrodeposition is a relatively easy technique to produce high-density nanocrystalline materials over powder consolidation methods those exhibits severe brittleness due to incomplete consolidation of the particle. In view of all this advantages, this technique has been commercialized for many industrial applications.

1.5 Nanocrystalline materials

Polycrystalline materials or amorphous materials with grain sizes less than 1μm, i.e. by reduction in grain size, by substantial increase in the volume fraction of grain boundaries and triple junctions, driven to a significant nanocrystalline (NC) materials, that has led to a material of choice with improved physical, chemical, electrochemical and mechanical properties.
Nanostructured materials engineering has enabled the possibility of designing environmental friendly anti-corrosion coatings which can last much longer compared to traditional coatings.\textsuperscript{51} Nanocrystallization, has of significant importance in surface chemistry that changes the growth process of the passive film, which improves the formation of compact film.\textsuperscript{52} In general, the corrosion resistance of nanocrystalline materials in aqueous solutions is of great importance in assessing a wide range of potential future applications.\textsuperscript{53}

1.6 **Key role of Additives**

An addition of small amount of substance to the plating baths, results in the improved surface properties of metallic deposition. That substance is named as additive. The primary role of these additives is to influence the factors affecting deposition process so as to get a bright coating on the substrate and considerable attention has been directed toward the development of effective additives/ brighteners to generate smooth and leveled bright deposit capable of providing higher corrosion resistance.\textsuperscript{54} The success of electroplating depends to a large extent on the type of additives introduced in plating baths. These additives are classified as primary and secondary, which always in combination produce bright deposit on an initially dull substrate or which maintains brightness on an initially bright substrate.\textsuperscript{55} Most of the primary additives are surfactants (wetting agents, levelers, and grain refiners). The function of the primary additive is to impart leveling and smoothness to the deposit. The typical examples are cationic (CTAB—cetyl trimethyl ammonium bromide), anionic (SDS—sodium dodecyl sulfate), and nonionic (Triton X-100, poly ethylene glycols PEG) surfactants. Cationic surfactant-like CTAB with positively charged head group interacts electrostatically with the electrode surface and thus get adsorbed on the active sites, modifying the crystal growth mode, tailors the morphology and refining grain size of the deposit.\textsuperscript{56} The secondary
additives are the organic compounds such as aromatic and aliphatic aldehydes, ketones, sulfur containing compounds, and alkyl and aryl ammonium salts., that influence the chemical composition, morphology and microstructure of the deposit, imparting good leveling and brightening effect on deposits by hindering or even inhibiting the electrodeposition process. These secondary additives interact synergistically with primary additive giving mirror bright finishing. Synergistic action exerted by mixture of additives enhances interaction between them and their adsorption (or incorporation) in the deposit.\textsuperscript{57} The concentration of additives ranging from 100 uM to 10 mM prevents the formation of whiskers or dendrites from growing, by adsorbing preferentially on the top of the dendritic growth sites, leading to a leveling effect, during the electrodeposition process.\textsuperscript{58} In case additives are also called as levelling agents, that are thought to be strongly adsorbed at the metal surface and to be surrounded by the depositing atoms and eventually incorporated into the deposit. A realistic model of levelling effect of organic additives was its non-reactive adsorption process.\textsuperscript{59} They play a major role in increasing the nuclear number, thereby creating competition between nucleation and crystal growth. The additives that were carried along with the metal ions towards the cathode cover the reduced metal nuclei, facilitates the formation of fresh nucleation sites, preventing the crystal growth on a particular metal seed, which is most beneficial to attain fine grained morphology, because it provides a larger number of nuclear sites on the deposit. As a result, additives control and modify the deposition overpotential and nucleation kinetics, enabling the production of coatings with high corrosion resistance and other functional properties.\textsuperscript{60-61}

1.7 OBJECTIVES

Nevertheless, lot of literature available on the electrodeposition of Ni-W alloys by electrodeposition technique using primary additives Sodium
Dodecyl Sulphate, saccharin sodium, sodium bromide and various composite materials like TiO₂, SiO₂, ultrafine alumina particles and studies on varying electrochemical parameters like temperature, current density and time, but there is lack of usage of organic aldehydes in Ni-W alloy plating baths and their effect on its properties.

The principal aim of this thesis is to enhance the corrosion resistance property and long term stability of Ni-W alloys, by using non-toxic organic additives in the plating baths. A simple, aqueous based, cost effective and viable electrodeposition technique has been used for the fabrication of corrosion defiant Ni-W alloy coatings. It was demonstrated that the usage of organic additives in the plating baths, improves the properties of the electrodeposits markedly. The efficacy of Ni-W alloy coatings in resisting corrosive species under stringent environment condition (0.2M H₂SO₄) and its underlying mechanism were discussed and proposed using electrochemical techniques. In addition, morphological, structural and related surface characterization techniques were done in accelerated laboratory conditions.