CHAPTER II
LITERATURE SURVEY AND SCOPE OF THE PRESENT RESEARCH WORK

Nanocomposite materials are of great interest for their enhanced properties than microcomposite materials. The rapid development of nanostructured materials in recent years resulted materials with different properties. One of the globally accepted and very easy methods of formation of nanocomposite coating is electrodeposition. Various kinds of nanocomposite coatings by using various nanopowders and metal matrixes can be produced by electrodeposition [1-10]. Direct current (DC) electrodeposition methods are commonly used for the fabrication of metallic as well as composite coatings. In general, the composite coatings have better microhardness as well as wear resistance [11-15]. Direct current electrodeposition methods are very simple with a constant applied current. The processes are often associated with slower deposition rates and coating defects. Pulse current (PC) and Pulse reverse current (PRC) electrodeposition methods are attracted significant attention to improve the deposition rates and microstructure of the coatings with enhanced mechanical and corrosion properties [16,17]. The DC, PC and PRC electrodeposition methods are used to prepare the metallic coatings. The enhanced microhardness values of PC electrodeposited nickel composite coating compared to DC electrodeposition have been reported [18]. Tribological and mechanical properties of nanocrystalline copper coating by using DC and PC electrodeposition methods were studied [19]. The copper coatings deposited by PC electrodeposition technique has exhibited higher hardness and better wear resistance compared to DC electrodeposited coatings. Pure nickel coatings deposited by PC and PRC techniques have showed better corrosion resistance compared
to DC electrodeposited coatings [16]. Nickel matrix composite coatings reinforced with a variety of reinforcements (Al$_2$O$_3$, SiC and ZrO$_2$) were reported. The nickel composite coatings are expected to increase the abrasion resistance of metal surfaces in microdevices. The effect of reinforced particle content of the electrolyte bath on the microstructure, tribological properties and level of reinforcement in the PC electrodeposited Ni-Al$_2$O$_3$ composite coatings have been investigated [20].

2.1 Ni-W ALLOY COATINGS

Nickel based alloys are used in a wide variety of applications for aerospace, energy generation and corrosion protection especially in an environment where materials have to withstand high temperature and oxidizing conditions [21,22]. Tungsten alloys are known for their excellent mechanical and tribological properties. Lowe, et al.[23] found that, the hardness of Ni-W alloys is two to three times higher than that of pure electrodeposited Ni. Nickel-tungsten layers with 10-weight % W resulted in microhardness (Vickers hardness) of 600 HV. Annealing at 650 ºC has increased the hardness produced values upto 800 HV. Younes et al.[24] indicated that, the concentration of W in the plated alloy has a major effect on the mechanical and chemical properties such as hardness, abrasion resistance and improved corrosion resistance at high temperatures. Also, Singh, et al.[25] also reported the microhardness of Ni-W deposits was found to increase with an increase in tungsten content in the alloy. Obradovic et al. [26] reported that, Ni-W alloys exhibit enhanced properties such as corrosion resistance, wear resistance and catalytic activity for H$_2$ useful in practical applications. They could also be used for magnetic heads, bearings, magnetic relays, catalysis of the processes of oxygen and carbon containing components of tungsten, electrodes for hydrogen energetics etc. Studies have shown that, Ni-W electrode materials accelerates the hydrogen evolution from alkaline solutions [27]. Tungstate
alloys with iron group elements are of interest in scientific and industrial applications in compositionally modulated multilayers (CMM), when these alloys could have altered magnetic properties for high speed and high density magnetic recording [28].

Electrodeposited amorphous nickel-tungsten alloy coatings having more than 44% W are found to possess superior properties making them one other potential alternative for hard chrome plating. These amorphous coatings were found to possess a high melting point (which made them more stable and heat resistant), high rigidity, abrasion resistance, and erosion resistance [29-35]. The characteristics of the coatings may change with the nature of the substrate and hence the substrate has to be prepared. Electrodeposited Co-W alloy and Co-W-WC nanocomposite coatings were produced and investigated under dry and wet sliding conditions [36]. The electrocatalytic efficiency was measured by using quasi-potentiostatic, galvanostatic and impedance spectroscopy techniques for the Ni-W catalyst obtained by in situ electrodeposition in an alkaline solution [37]. The mechanism of induced deposition of W in a Ni-W alloy formed electrochemically from ammonia-citrate electrolytes was studied [38]. Electroless coatings of Ni-P and Co-P, modified by introducing additional elements such as Zn and W were reported [39]. Nano crystalline Co-W alloy coatings were produced by dual-pulse electrodeposition from aqueous bath [40]. The influence of complexing agents and pH value on the crystal structure, morphology and hardness of the electrodeposited Co-W coatings were simultaneously investigated. In addition, the tribological properties of Co-W electrodeposits from different baths with different complexing agents or pH were studied [41]. Tribological and corrosive characteristics of binary and ternary alloys electrodeposited from Co-W, Fe-W, Co-Mo-P and Co-W-P citrate solutions were studied [42]. In the electrodeposition of iron-tungsten alloy from citrate electrolytes, the discharge of iron ions have occurred from the three valence
state. Increase in the sodium tungstate concentration in the electrolyte has contributed to the co-deposition of tungsten [43]. Nanostructured nickel-21 at% of tungsten alloy were electrodeposited on the copper substrate [44]. Bath chemistry, additives and operating conditions on the chemical composition, microstructure and properties of Ni-W alloy deposited from citrate-containing baths were investigated [45]. Ni-W alloy was deposited from acetate electrolyte [46]. The phase composition of electrodeposited Co-Ni-W alloy and the microstructure of amorphous films of this system on submicro and nanolevels were investigated [47]. Belevskii et al., [48] have studied the electroconductivity of the citrate solutions used to obtain the cobalt-tungsten coatings. Nanocrystalline Co-W coatings with 13-36 at% of W were obtained from citrate-borate electrolyte under DC and PC plating conditions at various at pHs [49]. Electrodeposition of Co-W alloy coatings from a citrate electrolyte with brightening and smoothing additives was investigated [50]. Effect of duty cycle, pulse frequency, Nano / micro mechanical and corrosion behaviour of the pulse electrodeposition of Co-W coatings were studied [51]. H.W.He et al. [52] have studied the Cu-Ni-W alloy by DC electrodeposition. Electrodeposited Ni-W alloys from nickel sulphate bath in the presence of various complexing agents were studied. The investigation has included the measurement of the current efficiency, determination of the tungsten content in the electrodeposits, voltammetry studies and characterization of complex formation by UV spectrometry [53]. Thermally stable LIGA materials for high temperature MEMS applications LIGA Ni-W layers and micro testing samples with different compositions of tungsten were deposited [54]. Nanocrystalline Ni-W alloys were prepared by electrodeposition and investigated their structure and contact-mechanical properties [55]. Morphological and chemical characterizations of Ni-W coatings in cross section have to estimate the degree of their homogeneity and to learn about the chemistry of the
coating/substrate interphase [56]. Nanocrystalline Ni-W alloy electrodeposits with finely dispersed micrometer-sized array through-holes were prepared by using the UV lithographic techniques [57]. Deformation and fracture characteristics of the electrodeposited nanocrystalline Ni-W alloy with grain size of 8.1 nm were investigated [58].

Ni-W nanostructured alloy coatings were known to exhibit superior mechanical and chemical properties than nickel coatings. In 1947 Brenner et al. [59] have deposited Ni-W alloys from alkaline sodium citrate bath. Using the same plating bath in 1998, nano crystalline Ni-W alloys were deposited [60]. Direct current plating was used to deposit the nanocrystalline Ni-W alloy deposits [61–69]. At high temperatures, Ni-W and NiW₂ alloys were also deposited with increased cathodic current efficiency [70,71]. Crystalline sizes were decreased from 7 to 2.5 nm when the wt% of W increased in the alloy. Many plating baths were alkaline (pH 7–9) with the addition of complexing agents such as sulphamate, ammonical citrate [72]. Pulse and pulse reverse plating techniques and its applications were reviewed [73]. Using sodium citrate as a complexing agent [74], Ni-W alloy coating was deposited by pulse plating method. A range of 65-140 nm grain sizes were obtained for 15-30 at.% of W in the alloy, when the pH of the bath was adjusted to 7. Ni₁₇W₃ phase was observed in the Ni-W alloy, when the pulse plating bath pH at 6. Crystalline sizes of 11-23 nm were seen in the alloy deposits [75]. Corrosion resistance behaviour of Ni-W electrodeposits was studied in NaCl and H₂SO₄ solutions. In the nanocrystalline Ni-W alloy as the grain size decreased to 15 nm, corrosion current densities decreased in 3.5% NaCl solution and increased again with the decrease in crystal size upto 5 nm [64,68,69,76,77]. Standard neutral salt spray tests on nanocrystalline Ni-W coatings demonstrated that, it can effectively shield the base metal steel [78]. Studies on reverse pulse electrodeposited nanocrystalline Ni-W alloy in 3.5 wt% NaCl at pH 3 and 10 revealed that the
corrosion rate of the alloy increased with the reduction of grain size in alkaline solution but decreased with the reduction in grain size in acidic solutions [79].

2.2 TiN BASED Ni-W NANOCOMPOSITE COATINGS

Composite electroplating is a method of co-depositing fine particles includes as metallic, non-metallic compounds or polymer into the plated layer to improve material properties such as microhardness, lubrication, dispersion hardening and corrosion resistance etc.. Pulse plating is an established method of electrodepositing metals and its alloys it significantly affects the mechanism of metal crystallization. The pulse parameters (such as peak current density, duty cycle and frequency) have influenced the adsorption or desorption of a species in the electrolyte and surface energy makes them less thermodynamically stable than the large grains. Therefore, resembling as in bubble coalescence, small grains tend to re-crystallize. Metals deposited by a PC technique have less absorbed hydrogen than those produced using a continuous current, causing desorption during the off period [80].

TiN nanoparticles have electrical and thermal conductivity and good corrosion resistance. Therefore, TiN coatings on stainless steel were used as bipolar plates of polymer electrolyte membrane fuel cells [81-83]. Ni-W amorphous coating was expected to apply to glass forming tools due to its high hardness, superior mechanical properties, corrosion resistance and the excellent release property [84]. Ni-W matrix composite coatings containing nano-sized Al₂O₃ particles were prepared under pulse plating procedure to study their tribological performance. The effect of the concentration of Al₂O₃ in the plating bath, the co-deposition percentage of Al₂O₃ embedded particles, the plating parameters and the microstructure of the deposits on the wear behavior of the composites, were investigated [85]. Ni-W-SiC nanocomposite coatings were prepared by the electrodeposition in a Nickel-Tungsten plating bath containing SiC nano-
particles [86]. $\text{La}_2\text{O}_3$ doped Ni-W composite coating were prepared [87]. High temperature corrosion behaviour of Ni-W-nano CeF$_3$ amorphous composite coatings were prepared on a stainless steel specimen [88]. Co-deposition of semiconducting molybdenum disulphide particles in Ni-W alloys was made using pulse plating [89]. Ni-W alloy coatings with different amounts of CeO$_2$ were prepared by using composite plating and the high temperature tribological performances of the coatings against molten glass also investigated [90].

Xingzhong Guo et al [91] have investigated the influence of the nano-TiN addition on the sintering behaviour, microstructure and mechanical properties of silicon carbide ceramics. The effect of a multilayered Ti/TiN coatings on the corrosion resistance of orthodontic brackets made of NiTi were investigated in artificial saliva [92]. Ti-Cu-N nanocomposite films with gradually changed composition were obtained by simultaneous co-deposition of TiN by reactive arc evaporation and magnetron sputtering of copper. Structure investigations of nanocomposite films with different content showed gradual decrease of the TiN grains while no copper phase in the film containing over at 2 at % copper was revealed [93]. The oxidation behavior and mechanism of TiCrN coating deposited on a steel substrate by ion plating were studied [94]. Ni-TiN nanocomposite films were prepared by DC electroplating technique. The influence of the solution agitation speed, TiN nano particle concentration, current density, bath pH value and bath temperatures on the microstructure of electrodeposited Ni-TiN nanocomposite films were investigated. The anticorrosion properties of the Ni-TiN nanocomposite films were studied [95]. The corrosion behavior of the TiN coated D2 tool steel was investigated. The enhanced corrosion resistance was due to the synergetic effect of the packing factor and the thickness associated with the coating [96]. The cavitation-erosion resistance of TiN coating deposited on stainless steel X6CrNiTi18-10 by cathodic arc method at different cavitation intensity was evaluated [97].
PVD deposited TiN coatings were very efficient in increasing the tribological performance of tool steels and cutting tools but the low Ti-6Al-4V hardness provided sufficient load carrying capacity for a hard coating. Nanocomposite TiN-Ni coatings were produced by a duplex treatment on Ti-6Al-4V substrates [98]. H.Altun et. al [99] have deposited TiN coating on the magnesium alloys by cathodic arc deposition process and evaluated corrosion behaviour of the alloys in NaCl and Na₂SO₄ solutions. The effect of composite layers have produced by nitriding under glow discharge conditions and also by the plasma assisted physical vapour deposition (PACVD) TiN on high alloyed tool steel was studied [100]. The corrosion behaviour of medium carbon steel coated with two different types of coatings was studied: (i) multilayered coatings of Ti/TiN with a graded composition interface and (ii) Multilayered coatings of Ti/TiN with a sharp composition interface. In both cases the Ti was incontact with the steel substrate [101]. The cavitation resistance of 3.7 µm thick TiN coatings on three hardness of stainless steel was investigated [102]. The effect of the temperature and thermal exposure on the interphase behaviour of continuous fiber reinforced titanium metal matrix composites were studied [103]. Surface films of TiN and TiN/Ti deposited on Ti6Al4V alloy by arc ion plating was studied [104]. The electrochemical behaviour of [TiN/TiAlN]n multilayer coatings under corrosion-erosion conditions were investigated [105]. Antimony doped into TiN film by using hybrid physical vapor deposition method was investigated [106]. Friction and wear behavior of TiN, CrN and MoN with and without copper coating have been investigated [107]. A dense Al2319/TiN composite coatings were successfully prepared using cold spraying with mechanically blended powders [108]. S.V.Hainsworth et.al [109] have conducted the indentation and scratch experiments over a range of TiN films deposited onto different substrate materials. Hardness of the TiN/a-SiNx coating with different silicon contents was measured and
subsequently modeled using finite element calculations based on the properties of TiN and a-SiNx [110]. An adaptive solid lubricant coating layer capped with a holey TiN layer demonstrated a lower friction coefficient and wear rate than monolithic TiN or Adaptive coatings [111]. Studies on adhesion strength and high temperature wear behaviour of ion plating TiN composite coating with electric brush plating Ni-W interlayer deposited on a hot work die steel were made using a plate-on-ring test rig [112]. Liuhui Yu et al. have prepared the Ni-P-nano TiN coating on AZ31 magnesium alloys by electroless plating process and investigated the composition, morphology, structure, microhardness and wear resistance of the composite coatings [113]. Nano Ni-TiN composite coatings were deposited on 45 steel substrate by ultrasonic electrodeposition. Ultrasonication had great effect on TiN nano particles in composite coatings. Ni-TiN composite coatings have exhibited a dense structure [114]. TiN/Ni composite coatings were deposited on 7005 aluminum alloy by high speed jet electroplating and then proceed with PTA scanning [115].

2.3 TiO₂ BASED Ni-W NANOCOMPOSITE COATINGS

TiO₂ has potential applications in various industrial and domestic fields including metallic and organic coatings, catalysis as catalyst support, photovoltaic cells and waste water treatment. TiO₂ has also been used to reinforce metallic coatings and it improves wear resistance, hardness and other properties such as corrosion resistance [116, 117]. The influence of sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB) surfactant on the morphology, composition, texture and corrosion behavior of electrodeposited Co-TiO₂ coatings were investigated [118]. The corrosion protective properties of TiO₂ on 304 stainless steel have been investigated [119]. Many authors have prepared the metal matrix composite coatings reinforced with TiO₂ micron [120-122], submicron [122,123] and nanoparticles [122,124–129].
They have exhibited photoelectrochemical and photocatalytical behaviors [130,131] with improved mechanical properties [122,124,127]. TiO₂ co-deposition was carried out with Cu and Zn as the metallic components [132,133]. The co-deposition of TiO₂ particles in nickel matrix has improved the mechanical and corrosion properties [134–139]. The Ni-TiO₂ composite coatings were prepared on steel substrates through electrodeposition and its mechanical properties had been reported [140]. Various amounts of TiO₂ incorporation in Ni-P-TiO₂ nanocomposite coatings were electrodeposited on low carbon steel [141]. TiO₂ incorporation was carried out in Ni-Co alloy matrix. The microstructure and its corrosion property had been reported [142]. Titanium dioxide (TiO₂) thin films were deposited on aluminum foils by cathodic electrodeposition. Al₂O₃-TiO₂ (Al-Ti) composite oxide films were formed on aluminum foils by anodizing in 15 wt% ammonium adipate solution. The growth mechanism of the Al-Ti composite oxide film was discussed. It was found that the TiO₂ coating layer with anatase structure was obtained on aluminum foil after heat treatment [143]. TiO₂/SiO₂ nanocomposite materials were electrodeposited on transparent fluorine doped tin oxide coated glass by cathodic electrodeposition at room temperature [144]. Superhydrophobic surfaces have been obtained on 316L stainless steel with Ni-TiO₂ nanocomposite coatings by a facile electrodeposition process [145]. The influence of the anodic pulse current value on the structural and morphological characteristics of the as-deposited Zn and Zn-TiO₂ nanocomposite coatings by pulse reverse current electrodeposition have been investigated. It is expected that, higher anodic current values favour the formation of nanocomposites with high quantity of incorporated nanoparticles [146]. Using pulse reverse electrodeposition, stoichiometric growth of ZnTe onto the TiO₂ nanotubular template have been investigated [147]. Co-TiO₂ nanocomposite coatings with various contents of TiO₂ nanoparticles were prepared by electrodeposition in Co sulphate bath containing TiO₂.
nanoparticles. The influence of the TiO$_2$ nanoparticles concentration in the bath and the current density and of sodium dodecyle sulfate on the morphology, composition, texture, roughness and microhardness of the coatings was investigated [148]. The amorphous Ni-P layers containing crystalline TiO$_2$ was evaluated after annealing [149].

The friction and wear properties of electrodeposited Nickel–Titania nanocomposite coatings were studied. Titania nanoparticles in the nanocomposite coatings were controlled by changing the concentration of the suspending titania nanoparticles in the plating bath. As the particle concentration has increased from 0 to 100 g/l. The content of the TiO$_2$ particles in the nanocomposite coatings have increased the maximum incorporation percentage of 9 vol % at low current densities and low pH values. The concentration of the co-deposited particles has affected the grain size of metal crystallites and enhanced the quality of the preferred crystal orientation. TiO$_2$ nano-particles in the composite coatings were dispersed uniformly in the nickel matrix on the surface as well as, through the cross-section of the deposits and the incorporation of the nano-particles took place between the grains [150].

2.4 SnO$_2$ BASED Ni-W NANOCOMPOSITE COATINGS

Tin oxide is a semiconducting material with high thermal stability. It is used as a precursor material for tribofilm formation on the rubbing steel surfaces [151] fillers in organic coating on glass bottles [152] and for the fabrication of gas sensors [153,154]. Synthesis of monodisperse system of submicron sized particles of SnO$_2$ and their incorporation in the nickel matrix by the electrodeposition process have been investigated [155]. The role of isoelectric point of SnO$_2$ in the co-deposition process was highlighted. The electrodeposition of Ni-SnO$_2$ composite coating on steel substrates and the evaluation of its mechanical properties were reported. The effect of SnO$_2$ particle content on electrodeposited nickel coatings and the changes
in wear resistance, coefficient of friction and microhardness were investigated. Ikram ul Haq et al [156] have studied ZnO2/SnO2 composite films of electrodeposited on FTO substrate using pulse potential technique. The electrodeposition process of ZnO/SnO2 was investigated through cyclic voltammetry to explore the formation mechanism of ZnO2/SnO2 composite. To obtain nano sized SnO2 electrodeposition [157]. Electrochemical synthesis of nanoporous SnO2 was done to be used as a photo anode in dye sensitized solar cells. Nanoporous oxide was prepared by cathodic deposition of tin followed by anodic oxidation in tin dichromate solution [158]. Incorporation of SnO2 into MgO-spinel (M-S) and its relationship between the parameters of their enhanced mechanical and microstructure properties have been investigated [159]. A cerium doped ternary SnO2 based anode (CeO2-RuO2-SnO2 (Ce-Ru-SnO2)) was prepared by facile thermal decomposition technique [160]. The role of anions such as Cl, Br−, I− on the anodic dissolution peaks on Sn(II) and Sn(IV) and also on the cathodic peaks was studied. The effect of halide ions on the corrosion of tin has been investigated [161]. Pulse electrodeposited tin coatings (β-Sn, tetragonal) have been synthesized successfully from a simple non hazardous electrolyte [162]. Sn/SnO2 nanocomposite and nanocrystalline SnO2 coating from nitrate solution by chronoamperometry and pulse techniques were studied [163].

2.5 EFFECT OF HEAT TREATMENT OF NANOCOMPOSITE COATINGS

Tungsten fiber-reinforced nickel alloy composites have been investigated extensively as a possible material for advanced gas turbine engine blades [164-167]. Most work has been focused on the strategies for improving the high temperature strength of these composites. Strength degradation can occur due to recrystallization of the W fibers during processing or use at high temperature or due to formation of brittle phases at the Ni-W interfaces [168-170]. To improve the mechanical properties of MgO-spinel composites through addition of varying ratios of SnO2
were prepared. They had increased resistance against fracture and greater resistance against thermal shocks [159]. The hot corrosion kinetic curves of the various coating systems were obtained and the best hot corrosion properties at 700°C and 900 °C have been investigated. In addition, the corrosion process was intensified with temperature [171]. Composite coating with the Cr-rich interlayer exhibited the best property during alkali-sulphate-induced hot corrosion at 900 °C due to the outer dense Al₂O₃ scale has been investigated [172]. The Ni-Co film/Fe substrate systems were prepared by pulse electro-deposition with heat treatment at various temperatures [173]. High temperature oxidation behaviour of Pd-Ni-Al coating and oxidation kinetics characterization of aluminized coating on Ni-base super alloy have been investigated [174,175]. Ni-W-P matrix coatings were prepared on carbon steel surface by pulse electrodeposition and high temperature oxidation behaviour was investigated [176]. High-temperature oxidation of Ni-16 at % W coating electroplated on the steel substrate was studied at 700°C and 800 °C [177, 178]. The oxidation rates of nanocrystalline Ni-W coatings were similar.
AIM AND SCOPE OF THE PRESENT WORK

Tungsten based nanocomposite deposits are of technological interest. Electrodeposition of tungsten in the pure state has not yet been successful from their aqueous or organic solutions. Co-depositing tungsten with the group VIII metals was successful. Several authors have investigated the process of electrodeposition of tungsten with iron group metals in aqueous solutions. Ni-W alloy coatings instead of chromium based coatings, production of a uniform deposit with all the desirable properties of nickel-chromium coatings can be accomplished.

Ni-W nanocomposite coatings have a significant impact on the MEMS, Oil and Gas Industries. The Ni-W nanocomposite coatings are highly resistant to corrosion, good mechanical properties both at room and high temperatures. The important applications are the fabrication of rotating equipment parts, drilling equipments etc.

The aim of the present work is to prepare Ni-W alloy based nanocomposite coatings to improve the mechanical and corrosion resistance properties. In this direction, the preparation of Ni-W nanocomposites incorporated with ceramic nanoparticles like TiN, TiO$_2$ and SnO$_2$ by Direct, Pulse and Pulse reverse current methods.

The plating bath variables on the co-deposition such as bath composition, current density, pH and temperature have to be optimized.

The optimized composition of the electrodeposited Ni-W nanocomposite coatings are to be examined by energy dispersive X-ray analysis (EDAX).

The crystallite size and structure of the electrodeposited Ni-W nanocomposite coatings are to be examined by X-ray diffraction analysis (XRD). The surface morphology of the electrodeposited Ni-W nanocomposites are to be examined by scanning electron microscopy (SEM) studies and Atomic force microscopy (AFM).
The mechanical property of the electrodeposited Ni-W nanocomposite coatings are to be evaluated by Vicker's microhardness tester. The corrosion resistance properties of the electrodeposited Ni-W nanocomposites are to be evaluated in 3.5% NaCl solution by electrochemical impedance spectroscopy and Tafel polarization studies.
REFERENCES


