ELECTRODEPOSITION OF Ni-W, Ag-W AND Ag-Ni-W ALLOYS FROM THIOUREA CITRATE ELECTROLYTES

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ABSTRACT

Tungsten (W) alloys, such as Ni-W, Co-W and Fe-W are well recognized for their outstanding corrosion resistance, wear resistance and catalytic properties towards hydrogen generation. Nickel-tungsten alloys also have the potential to act as barrier layers for applications in the semiconductor industries, to prevent intermetallic diffusion of the conducting metal (e.g. Cu, Au, Ag) into the substrate, e.g. Si. In addition, Ag-W alloys have been materials of interest as potential alternatives to replace more expensive Au interconnects in electronic packaging.

Tungsten, unlike traditional metals, cannot be reduced into metallic form alone from its respective chemical salt, and requires the presence of certain inducing elements (e.g., Ni, Co, Fe) exhibiting an induced codeposition mechanism to form alloys of W. This mechanism is however is not well understood and has been the topic of investigation for over two decades. Electrodeposition of Ag-W alloys and Ag-Ni-W alloys is also not well investigated, and there is an absence of understanding about the mechanism of deposition in the absence of known inducing metals, Ni in this case. Also, commercially electrodeposited Ag and Au alloys are cyanide based electrolytes which is an environmental and health hazard.

The objective of this research is to investigate the electrodeposition behavior of binary Ni-W, Ag-W and ternary Ag-Ni-W alloys from a cyanide free electrolyte. First, electrolyte deposition conditions; pH, applied current density, concentration of additives and temperature on the deposit composition and thickness of Ni-W thin films are examined. Electrolyte pH is a crucial variable, as it affects the metallic species present in the electrolyte. Increasing the electrolyte pH increases the W wt % in the alloy, while
increasing the electrolyte temperature resulted in improved metal deposition rates, thereby increasing the deposit thickness, as characterized by XRF. The effect of additives: sodium gluconate, boric acid and 2-butene-1,4-diol (BD), in the Ni-W electrolyte is examined using factorial design to increase the W wt % in the alloy, thickness and improve deposit appearance. Addition of boric acid is desirable to achieve uniform alloy composition, acting as a buffering agent. In the presence of BD, the Ni reaction rate is altered, depending on the electrolyte pH, and the presence of W ions in the electrolyte. Next, Ag-W thin film deposition as a function of W concentration and current density is investigated and a mechanism is presented. A high W wt % ~18 % was reported for the first time. Both concentration of W ions in the electrolyte and applied current density affected the alloy composition and surface morphology, as characterized by EDS/SEM. Increase in W ion concentration and current density increased the W wt % in the alloy and resulted in dendritic structures. An induced codeposition mechanism is believed to be responsible for the W deposition via a mixed-metal Ag-W intermediate. A first attempt on the electrodeposition behavior of ternary Ag-Ni-W alloy is presented. The presence of different Ni species in the electrolyte and its inducing effect on W deposition is investigated. Increase in Ni concentration in the electrolyte resulted in an increase in the Ni wt % in the alloy but did not increase the W wt % in the alloy, which is an interesting observation. An increase in concentration of citrate, a complexing agent, resulted in the formation of more stable Ni-Cit complex species, and resulted in decreased Ni wt % in the alloy. The applied current density and Ni concentration was found to have no distinguishable effect on the W deposition rates.
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1.0 INTRODUCTION

Tungsten alloys are well known for their outstanding properties, for example, Ni-W alloys are useful catalysts for electrolytic hydrogen generation, W imparts superior hardness and wear resistance to its alloys with Ni and Co, and W alloys have improved corrosion resistance compared to their codeposited counterparts [1]–[13]. The electrodeposition behavior of W alloys was coined by Brenner as “induced codeposition”, as W ions cannot be electrodeposited from its aqueous solution, but can be fully reduced if codeposited with iron group elements, such as Ni, Co and Fe [14]. A similar behavior occurs with Mo and the iron-group elements. Although a lot of work has been done towards investigating the mechanism of induced codeposition [8]–[10], [15]–[18] their reaction mechanism are not yet well understood. Younes et al. [18], [19] and Gileadi et al. [20] proposed a mixed intermediate soluble species [(Ni) (HWO₄)(Cit)]²⁻, which reduces together in parallel with the Ni reduction reaction to form an alloy. Podlaha et al. [21]–[23] assumed that Ni ions act as a catalyst for Mo reduction, regardless of the amount of hydrogen at the electrode surface and observed that deposition conditions for a given Ni-Mo deposit composition can occur at both low and high current efficiency, thus concluding that the side reaction may play a role in the codeposition, but perhaps not a governing one. Tungsten may behave similarly since it belongs to the same induced codeposition family.

The excellent conductivity of silver and its economic price compared to other precious metals make it an ideal replacement for electronics where high conductivity are required for faster electronics. However, the poor corrosion resistance of silver, along
with being a soft metal, warrants the need to improve the hardness and fabricate corrosion-resistant silver films [24]. Non-cyanide silver plating baths are very unstable and thus short lived, and hence electrolytes with cyanide are widely used in the industry to electrodeposit silver to date [25]. Over the years, many other electrolytes have been proposed as replacements to cyanide electrolytes, such as, iodide [26], thiourea [27]–[31] and thiosulfate [32]. Among the one’s investigated thiourea was considered to be the most effective chelating agent for Ag.

Silver being a noble metal compared to Ni or W, there exists a large difference in the reduction potential between Ni (−0.29 V\text{SHE}) and Ag (+0.799 V\text{SHE}), and a complexing agent is one way to shift the deposition potentials closer to achieve deposits with different alloy compositions. One key point is to employ a complexing agent which will selectively complex Ag and not Ni, the specific complexation of thiourea with Ag compared to Ni ions satisfies this condition.

The work presented here is devoted towards the advancement in the field of electrodeposition of binary, Ni-W, Ag-W alloys, and ternary Ag-Ni-W alloys. This dissertation will address the deposition parameters required to tailor the deposit composition for different applications. The electrodeposition of Ag alloys by replacement of commonly used cyanide electrolytes in the industry is another key feature of this work.
2.0 CRITICAL LITERATURE REVIEW

Ni-W alloys, and Ag alloys with Ni or W, can be fabricated by a variety of methods such as sputtering, electron beam evaporation and electrodeposition. The electrodeposition route can be cost effective compared to other techniques, and can easily be applied towards more complicated substrates such as recessed vias. Tungsten in pure form is known to be the strongest metal present on the periodic table, with the highest tensile strength of 1510 MPa. Tungsten is also has the highest melting point (3422 °C) and the lowest coefficient of thermal expansion (4.5 µm/mK) of all known metals. W alloys in general are also known for their superior corrosion resistance [1–4], outstanding wear resistance [35–38] and improved hardness [1], [2], [39]. In this chapter a review of the literature relevant to the electrodeposition of Ni-W and Ag alloys, its applications, and the various advances towards tailoring its properties are presented.

The electrodeposition of pure tungsten (and similarly Mo) has been attempted as early as 1930’s from aqueous solutions. However, attempts to achieve thick deposits of pure tungsten have been unsuccessful, possibly due to the formation of an oxide layer on the cathode surface which could not be further reduced into metallic tungsten [40]. Holt et al. [41] showed that tungsten electrodeposition could be achieved in the presence of certain metals (Co, Ni, Fe) with tungsten content as high as 50 wt %. This phenomenon is known as “induced codeposition” and was first coined by Brenner in 1963 [14].
2.1 **Induced Codeposition Mechanisms with Tungsten Alloys**

A significant amount of scientific work has been done to elucidate the deposition mechanisms and operating parameters towards the deposition of W and Mo with iron-group metals. In this section, literature pertinent to the work done towards refractory alloys, W and Mo, with iron group metals (Fe, Co, Ni) will be reviewed.

Many theories on the mechanism of induced codeposition have been proposed after the behavior was first recognized in the early 1930’s. Holt and Vaaler [42] were the first group to describe the reduction mechanism of tungsten codeposition with iron-group elements. They proposed a catalytic reduction mechanism in which the iron-group metal reduces first and the solid metal layer acts as a catalyst for tungsten reduction.

\[
\text{Me}^{2+} + 2e^- \rightarrow \text{Me}
\]

\[
\text{WO}_4^{2-} + 8\text{H}^+ + 6e^- \rightarrow \text{W} + 4\text{H}_2\text{O}, \quad \text{Me} = \text{Fe}, \text{Ni}, \text{Co}
\]

According to Golubkov and Yur’ev[43], during Mo electrodeposition with Fe and Ni, the Mo ions from solution form a layer of insoluble oxides and hydroxides on the surface and the presence of Fe or Ni affects the structure and chemical composition of the oxide or hydroxide layer by weakening the Mo-oxygen bond and allowing it to further reduce to solid state.

Chassaing et al. [16] proposed a multi-step reduction of Mo to an intermediate Mo (IV) oxide layer which was further reduced to solid metal in the presence of iron-group metals. This theory was supported by an *ex situ* chemical analysis of the oxide, determined as MoO$_2$Ni$_4$, which inhibits hydrogen evolution, and further reduces to the Mo-Ni alloy.
Clark and Lietzke [44] presented a different model which suggested that the tungstate was partially reduced followed by a catalytic reduction of this layer, in the presence of iron-group metals. Without the presence of the inducing element the tungstate would remain partially reduced.

Younes and Gileadi [18] and Younes-Metzler et al. [10] extensively studied ammoniacal citrate electrolytes. They introduced a hypothesis of a mixed ternary complex species and implied that this complex was the precursor for W deposition. The formation and deposition reactions are shown below.

\[
[(\text{Ni})(\text{Cit})^- + [(\text{HWO}_4)(\text{Cit})]^{4-} \rightarrow [(\text{Ni})(\text{HWO}_4)(\text{Cit})]^{2-} + \text{Cit}^{3-}
\]

\[
[(\text{Ni})(\text{HWO}_4)(\text{Cit})]^{2-} + 8e^- + 3\text{H}_2\text{O} \rightarrow \text{NiW} + 7\text{OH}^- + \text{Cit}^{3-}
\]

An upper limit in the tungsten content was observed, which was about 50-60 wt% for Ni-W alloy deposition from an ammonia-citrate electrolyte [45]. However, in the absence of ammonia this upper limit was increased up to 76 wt% tungsten in the alloy deposit; this was accompanied by a drop in the faradaic current efficiency [8]. Weston et al. [46] used UV spectroscopy and examined Co-W alloys from a gluconate electrolyte. They assumed significant quantities of a mixed (Co-gluc-WO$_4^{2-}$) complex could occur, consistent with work done by Younes and Gileadi [10], [18]. A study of Co-W alloys using cyclic voltammetry by Aravinda et al. [47] also proposed the reduction of tungsten from a ternary Co-W complex, while the reduction of Co occurred via a two-step reduction with Co$^{2+}$ ion as an intermediate. An increase in tungsten content is expected with an increase in the concentration of tungsten ions in the solution.
Podlaha and Landolt [22] examined the codeposition behavior of Mo with Ni, Fe and Co which may be extendable to the Ni-W system [23]. Their premise builds on the previous observations that an intermediate at the electrode surface occurs, but experimentally there was no consistent trend with the generation of hydrogen. Thus it was assumed that the role of hydrogen was not a dominating one. Also, they experimentally observed that when the inducing ions, such as a complexed nickel-citrate species, was in a low concentration in the electrolyte it limited the reduction rate of molybdate ions. Additionally, when the nickel reduction rate was under a mass transport control, the molybdate reduction rate mimicked the same transport behavior, despite being in excess in the electrolyte. In order to describe these observations a model was proposed where the molybdate reduction proceeds via an adsorbed intermediate step, treating the iron-group ion as a catalyst.

$$\text{NiCit}^+ + \text{MoO}_4^{2-} + 2\text{H}_2\text{O} + 2e^- \rightarrow [\text{NiCitMoO}_2]_{\text{ad}} + 4\text{OH}^-$$

$$[\text{NiCitMoO}_2]_{\text{ad}} + 2\text{H}_2\text{O} + 4e^- \rightarrow \text{Mo}_{\text{solid}} + \text{NiCit}^-$$

$$\text{NiCit}^- + 2e^- \rightarrow \text{Ni}_{\text{solid}} + \text{Cit}^{2-}$$

Sun et al. [9] extended the model proposed by Podlaha and Landolt by including the role of Ni ion and the Ni adsorbed intermediate into the previous adsorption model. They compared experimentally calculated reaction orders to their adsorption model and found that the Ni adsorbed intermediate species plays a critical role in inducing molybdate and tungstate reduction. The metal partial current density reduced as an effect of the adsorbed nickel onto the surface. They also found that the Mo reduction is favored
over the W reduction, which is attributed to the ability of the Ni-Mo intermediate to adsorb more readily than the tungstate intermediate.

The standard reduction potential for Ni (II) and WO$_4^{2-}$ for the electrochemical reactions is -0.257 vs. SHE and -0.591 vs. SHE, respectively. Complexing agents are often used to lower the difference between the reduction potentials between different metals. Several electrolyte formulations with various complexing agents are used for the electrodeposition of W and/or Mo with iron group metals; such as pyrophosphates[48], [49], acetate[50], and sodium citrate [9], [16], [21], [51]. Ammonia is commonly added to such electrolytes to adjust the pH, and also functions as a complexing agent. However, it was observed that the elimination of ammonia from the electrolyte resulted in higher W content in the deposit [8], [45].

### 2.2 Effect of additives on deposit properties

Additives are commonly added to Ni plating baths to improve its properties, such as, internal stress, corrosion resistance and brightness. Acetylenic compounds are known to be strong corrosion inhibitors in acidic solutions [52], and one such widely examined compound for corrosion inhibition of mild steel is 2-butyne-1,4-diol (BD) [53]. Many industrial electroplating electrolytes also contain certain organic additives with a sulphone functional group, such as, saccharin, thiourea, benzene sulfonic and amino benzene sulfonic acid, which reduce the internal stress of the deposited films [54]. Thiourea has been commercially used as a brightener, leveler, accelerator and stabilizer during nickel deposition [55]–[59]. This section will review the investigations done towards the effect of the above mentioned additives on Ni, and Ni-W plating.
2.2.1 Effect of 2 butyne-1, 4-diol (BD)

Nickel-tungsten is a promising alloy that may be of interest to replace the environmentally unfavorable hard chromium coatings, due to the satisfactory appearance of the coating, and the mechanical and anti-corrosion properties [7], [60]. The corrosion behavior of Ni-W alloys is well documented. For example, Yao, et al. [4] found that Ni-W is more corrosion resistant than stainless steel 304 in acidic media. Stepanova and Purovskaya [61] investigated the dissolution of different compositions of Ni-W alloys and found that an alloy having a composition of 28 wt% tungsten had the most favorable results.

Corrosion protection by organic inhibitors is mostly based on the modification of the surface properties of the metal alloy through adsorption of inhibitor molecules and the subsequent formation of a blocking layer. The inhibitive effects of BD on mild steel in sulfuric acid solutions was investigated by Hosseini and Arshadi [53]. They reported that the introduction of BD resulted in the formation of a thin inhibitor film on the steel surface after several hours of immersion and an inhibition efficiency upto 98 % was possible. Depending on the concentration of BD in the electrolyte, the internal stress on the films was found to vary [62], [63]. Zheng et. al [62] examined the effect of internal stress of Ni-W alloy in the presence of both saccharin and BD in the electrolyte. They found that an increase in BD concentration increased the tensile stress of the films, independent of the saccharin concentration in the electrolyte. This increase in internal stress was attributed due to the low current efficiency resulting from increased hydrogen evolution. However, little understanding is existent on the effects of BD on the deposition rates of nickel, tungsten and the side reaction during reduction. In chapter 4.2
(4.2.1- 4.2.5), the effect of concentration of BD, in an acidic and alkaline pH on the electrodeposition behavior of Ni, and Ni-W is examined.

2.2.2 Effect of Thiourea

Rogers et al. [55] examined the effect of current density on the incorporation of sulfur content in the deposit and found that the sulfur content was inversely proportional to the applied current density; higher sulfur content was obtained at low current density. They also reported that the deposits from non-agitated electrolytes appeared dull and contained less sulfur incorporation compared to deposits obtained from agitated electrolytes. This suggests that both the brightness and the sulfur incorporation could be diffusion controlled. Lead acetate was a commonly used stabilizer in the electroless plating electrolytes to prevent the decomposition of the electrolyte. However, in order to avoid the toxicity of the lead in a production environment, thiourea was used as a substitute. Baskeran et al.[56] examined the effect of thiourea along with the presence of other organic additives on the structure and formation of Ni-P alloys. He found that during Ni-P electroless plating, an increase in thiourea concentration up to 0.8 ppm, in the electrolyte accelerated the rate of deposition, while further addition of thiourea to 1 ppm inhibited the deposition rate. The enhanced deposition rate resulted in increased crystallinity and a coarse nodular morphology, compared to the smooth morphology obtained from lead acetate electrolytes.

One application of nickel and nickel alloys, in particular Ni-S alloys prepared by electroplating are functional cathodic materials for alkaline water electrolysis for hydrogen production [64], [65]. However, Ni-S alloys exhibit low mechanical properties and have poor adhesion to the substrate, due to micro-crack spresent in the
deposit [66]. Stress reducers such as thiourea, could act as a stress reducer. Furthermore, the presence of W as stated earlier exhibit excellent hydrogen evolution characteristics at low over potential. Yoshihara et al. more recently electroplated Ni-W-S and Ni-S electrodes using thiourea as a sulfur source and evaluated their hydrogen evolution capability. They reported improved hydrogen evolution behavior for the Ni-W-S electrodes compared to Ni-S electrodes. They also reported that the electroplated Ni-W-S electrodes were relatively stable compared to conventional Ni-S electrodes.

Mohanty et al.[59], however pointed out that, at high concentrations of thiourea (>40 mg/dm$^3$), a significant deterioration of Ni deposits is observed and a blackish rough deposits are obtained. An increase in sulfur content in the deposit is associated with an increase in thiourea concentration in the electrolyte. Dissociation of thiourea into other sulfur containing molecular fragments was also observed during Ni deposition. A depolarizing effect on the Ni deposition rate was observed up to concentrations of 10 mg/dm$^3$. A similar trend in behavior was also observed by Liang et al. [67], during electrodeposition of Ag-Ni alloys from a thiourea electrolyte.

However, thiourea (TU) is known to complex with Ag (I), and different complexes occur depending on the ligand:silver ratios in the bath [27], [29], [67]–[69]. Gómez[27] reported the use of thiourea (TU) for the electrodeposition of Ag, with the intent to move its reduction potential closer to the range of other transition metal reduction potentials to form alloys, and as a more environmentally friendly alternative to conventional cyanide electrolytes. TU was found to promote the formation of smooth, homogeneous, finer-grained Ag deposits within a range of low applied potentials. This was a significant finding since Ag tends to electrodeposit in a highly dendritic way.
Silver deposits fabricated from the TU electrolyte were shown to incorporate low sulfur content at low overpotential, while the sulfur content in the deposits increased when dendritic growth developed, at high overpotentials. Sulfur incorporation into a Ag-Zn alloy using a thiourea electrolyte was also reported [29] and the sulfur incorporation was attributed to TU hydrolysis driven by the increased alkalinity at the cathode surface from the parallel hydrogen evolution reaction. The smoothest morphology was obtained with the largest amount of sulfur incorporation. Also TU was used in a sulfuric acid electrolyte for Sn-Ag-Cu electrodeposition by Fukuda et al. [69] for solder applications and the TU addition was found to have a smoothing effect of the microstructure.

2.3  **Interest in Ag-W Alloys**

In this section a review of the work done on Ag-W deposition mainly for their applications towards the semiconductor industry has been presented.

The application of silver for ultra large scale integration is promising due to its low bulk resistivity (1.59 $\mu\Omega\text{cm}$), relatively high melting point and higher electromigration resistance compared to Cu, which is widely used in the down-scaling of interconnects. Suitable conductivities were reported for Ag fabricated by sputtering [70], [71] and electroplated thin films [72], while some drawbacks of Ag, such as corrosion in air and diffusion in SiO$_2$, could be avoided by using a suitable binary alloy such as Ag-W instead of pure Ag [73]. There are several methods to deposit thin metal films for interconnect applications, physical vapor deposition (PVD), chemical vapor deposition (CVD) and electrochemical methods (either electroless or electrodeposition). Among the different technologies, chemical methods are preferred for ULSI interconnects because of
their compatibility with the Dual damascene scheme that requires filling of high aspect ratio features [74].

Although Ag is noted for its extremely low bulk resistivity [25], it is susceptible to corrosion in the presence of weak oxidizing agents, has poor mechanical properties, and can diffuse into dielectric substrates, which limits its use in microelectronic and microelectromechanical systems. To this end, several investigators have developed electrochemical processes to deposit a small amount of tungsten with silver to improve its hardness and corrosion resistance to air. Shacham-Diamand et al. [75] and Bogush et al. [74] electrolessly deposited 1-3 at % W (up to ~ 5 wt % W) with reported oxygen in the deposit. Hydrazine hydrate was used as a reducing agent with ammonia and acetic acid, or benzoate, to buffer the electrolyte and complex silver ions at high pH 10-11.5. A decrease in tarnishing of the surface in the presence of tungsten was observed, and the Ag-W film roughness was found to decrease slightly [76], [77]. The microhardness value was also affected by the presence of W, increasing up to 1.2 GPa for a W deposit content of 3.2 at % compared to a value of 0.61 GPa for Ag deposited under similar conditions. The resistivity increases over that of elemental Ag, but Glickman et al. [59- 60] have shown that the resistivity can be reduced with a subsequent vacuum annealing step. The higher resistivity with W was attributed to a porous structure, co-segregation of W and oxygen, and formation of non-metallic phases: Ag₅W₂O₇ and AgO, at the grain boundaries.

While the mechanism of the electrochemical deposition is not well understood there are some notable observations. Inberg et al. [24] observed in electroless deposition that the concentration of tungsten in the solid film reached a maximum of approximately
3.2 at % when the molar ratio of tungstate to silver ions, $[\text{WO}_4^{2-}]\cdot[\text{Ag}^+]^1$, was unity. Higher concentration of tungstate ions in the solution did not further increase the tungsten ion concentration in the solid. It is proposed that the mechanism during electroless deposition involves $\text{Ag}_2\text{W}_2\text{O}_7$ species adsorbed onto the electrode surface [73].

Recently, the electrodeposition of W and Mo with Cu has been reported in the literature [78], [79]. The Cu-W [78] alloys with W content above 10 at % (26 wt %) were deposited from alkaline citrate electrolytes in an excess of sodium tungstate compared to copper sulfate. The deposit structure investigated with TEM indicated Cu nanocrystals surrounded by an amorphous tungsten rich phase. The phase segregation is expected since W and Cu do not form thermodynamically stable binary alloys. Cu-Mo [79] was investigated with varying amounts of $\text{MoO}_4^{2-}$ and citrate as the complexing agent. Gotou et al. [79] found that the Mo content reached a maximum at 8.1 wt % with increasing amounts of molybdate in the electrolyte and then decreased with further molybdate concentration. The ratio of molybdate ions in the solution to the total metal ion concentration examined was $\geq 0.5$, so there were always more molybdate ions than copper ions. A similarity between Ag and Cu codeposition with a reluctant element, such as W or Mo, is that both Ag and Cu are noble elements. Without a large change in the reduction potential aided by complexation, deposits with an excess of the noble element would be expected. Reducing the concentration of the more noble metal ions (e.g., Cu, Ag), and thus creating a mass transport regime is also another way to prevent deposition of entirely the noble metal. A combined strategy is presented in Chapter 4.3 for Ag-W.
2.3 **Interest in Ag-Ni alloys**

Ag-Ni alloys are promising candidates for electrical contacts and switches [58, 59] and exhibit remarkable catalytic properties [57]. However, the Ag-Ni deposition system remains one of the least examined systems to date via electrodeposition synthesis [49, 60-62], while other methods used in the synthesis of these alloys include laser-deposition [63], vapor quenching [64], ion mixing [65] and electron-beam co-evaporation [66]. According to the phase diagram [67], Ag and Ni are immiscible in bulk form and even intermetallic phases were not observed at high temperatures. However, the alloying effect at the nano-scale level is quite different from bulk, since the heat of formation reduces with decreasing particle size and hence alloying these metals becomes a possibility. Another aspect of the Ag-Ni system is the large difference in reduction potential Ag (+0.799 V\text{SHE}) and Ni (-0.25 V\text{SHE}) [49], an important feature of thiourea especially while considering Ag-Ni deposition from the same electrolyte is that, while thiourea binds strongly to Ag+ ions, it form a weak complex with Ni2+ ions. This selective complexation becomes crucial to lower the large difference in redox potentials between.

Eom et al. [60], examined the deposition of the alloy in sodium citrate electrolytes. A shift in the Ag ion deposition potential to more negative values was observed in the presence of citrate. They identified pH to be a dominant factor to control the composition of the samples, as it affected the complexing of the metal ions with citrate. At low current densities (0.5 mA/cm2), dendrite formation was observed with a film composition of Ag60Ni40, and the microstructure transformed to a granular deposit with increasing current density, which correspondingly increased the Ni content. The
dendrite formation was attributed to the low concentration of Ag ions in the electrolyte. A low concentration of Ag ions in the electrolyte causes a depletion of ions on the cathode surface due to mass transport limitation and causes non-uniform nucleation of Ag. A similar dendrite formation was also reported by Zhou et al. [71].

Santhi et al. [62] examined the microstructure of the Ag-Ni alloys with different ratios of Ag:Ni (1:10 and 1:20) in the electrolyte and using pulsed galvanostatic deposition at different current densities (40, 50 and 70 mA/cm²). They used thiourea as the complexing agent for Ag and sodium gluconate for complexing Ni. They reported similar findings as Eom et al. [60], the high current densities resulted in Ni rich films with granular morphology. The low Ag content (17-5 wt %) in the samples was attributed to the low concentration of Ag ions in the electrolyte and that composition was a clear function of the current density and compositional ratio of the metals in the electrolyte. The presence of sulfur was also identified in the samples (6-10 wt %), which is caused due to the adsorption of thiourea from the electrolyte. Similar sulfur inclusion was also reported by Garcia Torres et al. [54]. Composition analysis of two separate regions of the Ag-Ni alloy, one sheet-like structure and another with dark spherical particles, revealed that the sheet-like region was Ni rich (100 wt %), while the black particles indicate Ag Ni (71 at % Ag and 29 at % Ni) alloy, embedded on the sheet-like structure.

Electrodeposition of ternary Ag-Ni-W alloys from a single stable electrolyte has been presented for the first time in chapter 4.4. The addition of Ni to a Ag-W electrolyte was examined using polarization curves and partial current density calculations. Ag-rich deposits were obtained at low current densities (<20mA/cm²), while increase in current
density resulted in an increase in the Ni content. The effect of citrate ion concentration in an Ag-Ni-W electrolyte was also investigated. Using a complexation model for a fixed Ni-W ion ratio in the electrolyte, the effect of different Ni-citrate complex species on deposition behavior of W was investigated.
3.0 EXPERIMENTAL

The overall goal of this research was to investigate the effect of additives on Ni-W deposition behavior and to develop a cyanide free single electrolyte for Ag-Ni-W ternary alloy deposition.

3.1 Electrolytes

All electrolytes were prepared using de-ionized ultra-filtered (D.U.I.F) water from Fischer Scientific. Tri-sodium citrate was used as a complexing agent for Ni and W ionic species, while thiourea (TU) was used for selective complexation of Ag. The electrolytes, deposition conditions, deposit characterization conditions used are presented in the first part of this section. In section 3.3, the cell design and setups used for electrodeposition of Ni-W, Ag-W and Ag-Ni-W alloys are discussed.

3.1.1 Ni-W Electrolytes

The base electrolytes used for Ni-W electrodeposition for sections 4.1 and 4.2.1-4.2.5 of this study are presented in Table 1 and Table 2 respectively. The pH of the electrolyte was varied between 2 and 8. The electrolyte concentration used in section 4.2.6 is presented in Table 3, the electrolyte was maintained at pH 2.
Table 1. Base electrolyte used for Ni-W electrodeposition (Section 4.1-4.2.5)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Sulfate</td>
<td>0.1</td>
</tr>
<tr>
<td>Sodium Tungstate</td>
<td>0.15</td>
</tr>
<tr>
<td>Tri-sodium Citrate</td>
<td>0.285</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>0-0.5</td>
</tr>
<tr>
<td>Boric acid</td>
<td>0-0.5</td>
</tr>
<tr>
<td>Thiourea</td>
<td>0-0.325</td>
</tr>
</tbody>
</table>

Table 2. Electrolyte used for Ni-W electrodeposition (Section 4.2.1-4.2.5)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Sulfate</td>
<td>0.1</td>
</tr>
<tr>
<td>Sodium Tungstate</td>
<td>0.15</td>
</tr>
<tr>
<td>Tri-sodium Citrate</td>
<td>0.285</td>
</tr>
<tr>
<td>2 butyne, 1-4 diol</td>
<td>0-0.005</td>
</tr>
<tr>
<td>Boric acid</td>
<td>0-1</td>
</tr>
</tbody>
</table>
Table 3. Base electrolyte used for Ni-W electrodeposition (Section 4.2.6)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Sulfate</td>
<td>0.5</td>
</tr>
<tr>
<td>Sodium Tungstate</td>
<td>0.15</td>
</tr>
<tr>
<td>Tri-sodium Citrate</td>
<td>0.5</td>
</tr>
<tr>
<td>Thiourea</td>
<td>0-0.650</td>
</tr>
</tbody>
</table>

3.1.2 Ag-W Electrolytes

The base electrolytes used for Ag-W electrodeposition for this part of the study is presented in Table 4. The amount of sodium tungstate was varied in this study to examine the effect of complexed tungstate-citrate ions on the electrodeposition of Ag-W alloys. The pH of the electrolytes was maintained at a value of 2.

Table 4. Electrolyte used for Ag-W electrodeposition (Section 4.3)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver Sulfate</td>
<td>0.05</td>
</tr>
<tr>
<td>Sodium Tungstate</td>
<td>0.03, 0.075 and 0.15</td>
</tr>
<tr>
<td>Tri-sodium Citrate</td>
<td>0.285</td>
</tr>
</tbody>
</table>
3.1.3 Ag-Ni-W Electrolytes

The base electrolytes used for Ag-Ni-W electrodeposition is presented in Table 5. The pH of the electrolyte was maintained at a value of 2.

Table 5. Base electrolyte used for Ag-Ni-W electrodeposition (Section 4.4)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver Sulfate</td>
<td>0.005</td>
</tr>
<tr>
<td>Sodium Tungstate</td>
<td>0.15</td>
</tr>
<tr>
<td>Tri-sodium Citrate</td>
<td>0.285</td>
</tr>
<tr>
<td>Thiourea</td>
<td>0.250</td>
</tr>
</tbody>
</table>

3.2 Deposit Characterization

The deposit thickness and composition was analyzed with a KEVEX Omicron energy dispersive X-ray fluorescence analyzer (XRF). The conditions for the analysis were optimized for heavy elements (i.e., Ag, W) and not for the light elements (e.g., S, O, C), at 40 kV, 1.5 mA, in air and with an acquisition time of 60 s. The surface morphology was examined using a scanning electron microscope (SEM) obtained using a HITACHI 4800 at two different magnifications (7 KX and 50 KX). The composition of the alloy was determined using electron dispersive spectroscopy (EDS) to include the detection of oxygen and sulfur in the deposits.
3.3  **Cell Design**

Different cell designs are available to examine the effect of a large number of variables on the electrodeposition process. On a micro scale level, one could investigate the electrochemical kinetics of a particular reaction or the influence of different additives on the kinetics of deposition, thickness and deposit composition. A Hull setup is useful when surveying deposition conditions over a wide range of applied current densities in a single experiment, saving cost and time [80]. Vertical air bubbling is an added feature which can help examine the effect of agitation on the electrodeposition process. Another type of Hull cell is the rotating cylinder Hull cell, which is useful in cases where mass transport becomes important [81]. In this section a review of both the cell designs and its application to our system of investigation is presented.

3.3.1  **Conventional Hull Cell**

A conventional Hull cell is useful when surveying plating conditions over a wide range of applied current densities. A current distribution develops when the reaction rates are not mass transport controlled and when ohmic effects dominate, with one end of the electrode having a high current density and the other end that is farthest from the counter electrode, having a lower current density. To help eliminate mass transport dominated reactions the cell is agitated with air bubbling. A typical Hull cell is shown in Figure 1(a) where the cathode is at an acute angle with the counter electrode. When the two electrodes are parallel, a constant current is promoted as shown in Figure 1(b) and is used
for generating polarization curves. The dark circles in Figure 1 are to represent the position of the air vents for jet agitation.

![Figure 1](image.png)

**Figure 1. Cell configurations - (a) Hull cell used for current distribution analysis, (b) parallel configuration used for polarization and constant current density analysis.**

Agitation of the electrolyte in the Hull cell is done by using air, bubbling close to the surface of the cathode to ensure uniform mixing. A flow meter is used to monitor the entering feed rate of air into the Hull cell. The primary purpose of any form of agitation to the electrolyte is to eliminate or minimize concentration gradients near the electrode surface to avoid mass transport limitations. Air agitation can help then to control the boundary layer thickness during deposition, which is a crucial factor when depositing alloys involving diffusion limited species. In the parallel configuration mode, the anode and cathode are place parallel to each other as shown in Figure 1(b), and the effect of current density is examined under the same mixing environment. Copper plates from ESPI metals were used as working electrodes with an area of 47 cm² and a rectangle piece of Pt was used as the anode. All substrates were cleaned in dilute H₂SO₄ (10 vol %) in order to remove any copper oxides and cleaned in D.I.U.F water before deposition. The deposition was galvanostatically controlled using a Solartron potentiostat/function.
generator model 1287A. An average cathodic current density of 50 mA/cm² was applied for duration of 30 min at room temperature for all the Hull cell experiments for section (4.1-4.2.4). The average current density used for section 4.2.5 was 10 mA/cm². Since the silver concentration in the electrolytes is low, in the case of Ag-W and Ag-Ni-W electrodeposition (section 4.3 and 4.4), the mass transport effects will be considerable and the deposition will depend heavily on the hydrodynamic environment during deposition, a rotating cylinder electrode setup was used for those experiments.

3.3.1.1 Characterization of air agitation in a Hull cell

The characterization for the Hull cell was done in order to demonstrate the concept of effect of agitation (air) on the limiting current density of any metal in low concentrations. For this purpose, a ferricyanide reduction reaction was examined with varying flow rates (air bubbling). A potassium cyanide electrolyte $K_3Fe(CN)_6$ (0.02M), saturated with NaOH (0.5M) was used. The diffusivity of the species is taken as $D=7.1 \times 10^{-6}$. A ferricyanide reduction is a convenient system, because the reduction happens without undergoing a physical deposition on the surface of the cathode, multiple reactions can be run under different conditions; $[Fe(CN)_6]^{3^-} + e^- \rightarrow [Fe(CN)_6]^{4^-}$. In Figure 2, a polarization at a scan rate of 5 mV/s is shown, where the initial rise in current vs potential (0.2 to -0.1 V) is identified as the kinetic region for electrodeposition and is governed by the Butler-Volmer equation given by the expression:

$$i = i_o \left\{ \exp \left[ \frac{\alpha_n F \eta}{RT} \right] - \exp \left[ - \frac{\alpha_n F \eta}{RT} \right] \right\}$$

The current at the plateau region between -0.1 and -0.6 V is known as the limiting current density. This limiting current indicates that the reaction is now under mass
transport control. The limiting current density increases with increasing flow rate which is expected. The concept of limiting current in the literature is expressed by:

\[ i_L = -nFD \frac{c_s - c^b}{\delta} \]  \hspace{1cm} 3.2

At limiting current the surface concentration \( C_s \) drops to zero, since all the ions at the surface are reduced instantly and further increase in agitation, decreases the boundary layer thickness (\( \delta \)) near the cathode surface, increases the limiting current and increases the region for kinetic deposition. Furthermore, films deposited under limiting current density tend to become rougher and less compact, which is undesirable. In our experiments with Ag, we expect Ag to be under mass transport control, since the concentrations used in our electrolyte is relatively low compared to the Ni and W ions in the electrolyte. Also, since the reduction potential between Ag and Ni is large, by maintaining a low Ag concentration in the electrolyte, one can minimize obtaining Ag rich deposits.
Figure 2. Polarization curve for ferricyanide reduction with varying flow rates.

3.3.2 Rotating Cylinder Electrode

Another setup to maintain the hydrodynamic environment near the electrode surfaces is to use a rotating electrode. A three electrode cell design was used to galvanostatically deposit Ag-W alloys onto Cu rotating cylinder electrodes in a two compartment cell. The working rotating cylinder electrode (RCE) has a slightly recessed design in order to maintain a uniform current distribution near the electrode edge. The Cu substrate diameter was 0.62 cm and the recess was 0.45 cm from the edge of a cylindrical Teflon holder. The catholyte and anolyte was separated by a glass frit in the two compartmental cell. A Pt mesh was used as the counter electrode and Ag/AgCl as the reference. The Cu substrates were cleaned in 10% vol H₂SO₄ for 1 min, and rinsed in
deionized water before each experiment. Deposition was carried out at a rotation rate of 350 rpm, where turbulent flow is expected for duration of 10 min. The rotation rate was controlled using a Pine Research Instrumentation. Figure 3 shows a schematic of a rotating cylinder used for the electrodeposition of Ag alloys. A polarization scan at 10 mV s$^{-1}$ for each electrolyte was carried out and corrected for ohmic drop using electrochemical impedance spectroscopy. The current density was varied over a wide range (5 mA/cm$^2$ – 320 mA/cm$^2$) for duration of 10 min. The advantage of the rotating cylinder electrode over the conventional Hull cell is that there is a well-defined control over the hydrodynamic conditions. In cases, such as Ag deposition, where the boundary layer thickness plays a huge role in determining deposit composition, it becomes important to have better control over the mixing conditions.
Figure 3. Schematic of a rotating cylinder electrode setup
4.0 RESULTS AND DISCUSSION

In the first section of the results, the electrodeposition of Ni and Ni-W electrolytes with different additives are examined and compared (Section 4.1 and 4.2). The deposit metal composition and thickness were used to determine the partial current densities of the metals and the side reactions in order to characterize the electrodeposition process. The effect of additives on the electrodeposition process was investigated. In the second section (4.3), the effect of tungstate ion concentration in the electrolyte on Ag electrodeposition is examined. Polarization curves and partial current densities are used to characterize the changes in the deposit composition. In the third section (4.4) Ag-Ni-W alloys and its electrodeposition is examined for the first time. Here, the effect of Ni ion concentration on Ag-W deposition behavior and the effect of citrate ion concentration in the electrolyte, its complexing effect on Ni and W ions, is presented.

4.1 Factorial Design Approach for Ni-W Electrodeposition

One way to examine a system when more than two variables are involved is to use a factorial design approach. In this section, the effect of four variables; electrolyte pH, boric acid, sodium gluconate and temperature, and their interdependence on the Ni-W deposit composition and thickness are examined

4.1.1 Effect of pH, Boric acid and Sodium Gluconate

In our examination of Ni-W alloy electrodeposited from ammonium ion free, citrate electrolytes, in all five different variables were examined: pH, boric acid concentration sodium gluconate, thiourea concentration and temperature. In a non-factorial design approach, consisting of three variables, the first variable is changed while
the other two variables remain constant at a certain applied current density or potential. The second variable is then held constant and remaining two are varied, and so on. In this manner, a large number of experiments are required. For example, if only four values of each variable are planned, then for three variables, \(4^3 = 64\) experiments are required to assess if the variable increases or decreases the deposit composition and/or the resulting thickness for a given deposition time. Replicating the experiments should also be included, so that if each experiment is done three times, the total number of experiments becomes \(3 \times 4^3 = 192\) experiments.

In a factorial design approach [82] only two values of each variable, or factors, are selected, a low value (−) and a high value (+). All possible combinations of factors can be investigated in \(2^3\) experiments, with additional experiments for replication. In general, for \(k\) variables or factors, the smallest subset of experiments is \(2^k\).

Table 6 shows the eight combinations of experiments needed to assess how three factors affect the deposit outcome. The notations for these experiments are similar to those used by Montgomery, et al.[82] and reflect which variable is the higher amount. For example, the experiment notation “a” corresponds to electrodeposition carried out when variable A is at a high value but the other two variables B and C are at low values. For the first set of examination, the variable A = electrolyte pH, B = electrolyte concentration of boric acid and C = electrolyte concentration of sodium gluconate were considered. In contrast, experiment “bc” is conducted under conditions where the pH is low and the amount of boric acid and sodium gluconate concentration is high.
Table 6. A $2^3$ experimental design showing the low (-) and high (+) values of the different variables.

<table>
<thead>
<tr>
<th>Experiment notation</th>
<th>Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A pH</td>
</tr>
<tr>
<td>1</td>
<td>(-)</td>
</tr>
<tr>
<td>a</td>
<td>(+)</td>
</tr>
<tr>
<td>b</td>
<td>(-)</td>
</tr>
<tr>
<td>c</td>
<td>(-)</td>
</tr>
<tr>
<td>ab</td>
<td>(+)</td>
</tr>
<tr>
<td>ac</td>
<td>(+)</td>
</tr>
<tr>
<td>bc</td>
<td>(-)</td>
</tr>
<tr>
<td>abc</td>
<td>(+)</td>
</tr>
</tbody>
</table>

The influence of a variable on the desired outcome, such as deposit composition, can be assessed by “Effects,” which are parameters determined by taking the averages of the desired outcome values, such as wt% W, shown in Table 7. The effects are calculated for each variable and its interaction with other variables on the desired outcome. The number of replicates are designated as $n$, and the values of the outcomes, such as wt% W, are used for the corresponding experiments, a, b, c, ab, ac, bc and abc.

Table 7. Equations used to calculate the average value of the measured outcomes in the $2^3$ experimental design with $n$ replicates.

<table>
<thead>
<tr>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of a $\frac{1}{4n} \left[ (a + ab + ac + abc) - (1 + b + c + bc) \right]$</td>
</tr>
<tr>
<td>Effect of b $\frac{1}{4n} \left[ (b + ab + bc + abc) - (1 + a + c + ac) \right]$</td>
</tr>
<tr>
<td>Effect of c $\frac{1}{4n} \left[ (c + ac + bc + abc) - (1 + a + b + ab) \right]$</td>
</tr>
<tr>
<td>Effect of ab $\frac{1}{4n} \left[ (c + ab + 1 + abc) - (bc + a + b + ac) \right]$</td>
</tr>
</tbody>
</table>
The Ni-W citrate electrolyte for these experiments is mentioned in Error! Reference source not found., with two pH values: 2 and 8. The concentration of boric acid and sodium gluconate had values of 0 or 0.5 M. The primary objective from these experiments is to monitor the change in the W wt%. The cell setup of Figure 1 (b) was used to maintain the same hydrodynamic mixing environment. The deposition was carried out at an air agitation rate of 3 L/min and at an applied current density 30 mA/cm² for duration of 30 min. Each experiment was replicated 3 times and their average values were taken. Table 8 shows the summary of the factorial design experiments deposit pictures, optical images and their corresponding W wt %.

Table 8. Summary of the factorial design experiments, deposit photographs and W wt %

<table>
<thead>
<tr>
<th>Experiment notation</th>
<th>A pH</th>
<th>B Boric acid</th>
<th>C Sodium gluconate</th>
<th>Deposit Images</th>
<th>Optical images (50X)</th>
<th>W wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
<td></td>
<td></td>
<td>6.3 ± 1.6</td>
</tr>
<tr>
<td>a</td>
<td>(+)</td>
<td>(-)</td>
<td>(-)</td>
<td></td>
<td></td>
<td>57.7 ± 3.7</td>
</tr>
<tr>
<td>b</td>
<td>(-)</td>
<td>(+)</td>
<td>(-)</td>
<td></td>
<td></td>
<td>20.7 ± 4.5</td>
</tr>
</tbody>
</table>

Effect of \( ac \)

\[
\frac{1}{4n} [(b + ac + 1 + abc) - (ab + a + c + bc)]
\]

Effect of \( bc \)

\[
\frac{1}{4n} [(a + bc + 1 + abc) - (ab + b + c + ac)]
\]

Effect of \( abc \)

\[
\frac{1}{4n} [(a + b + c + abc) - (ab + ac + bc + 1)]
\]
The individual and combined effects determined from the values taken from Table 8 are plotted in Figure 4 and Figure 5. The results suggest that the electrolyte pH has a larger positive effect on the W wt% in the deposit, and this can be attributed to the change in tungstate species in the electrolyte which leads to an increase in the W wt %. Similar effects were seen by increases boric acid concentration however, it had a smaller influence compared to electrolyte pH. The addition of boric acid acts as a buffering agent and reduces the surface pH near the electrode, which prevents the reducing species near the surface from changing and hence leads to an increase in the W wt%. The adsorption of boric acid molecules onto the substrate, prevent the adsorption of H\(^+\) ions, thereby reducing the availability of active surface area for H\(_2\) formation and increasing metal reduction rate. The reduction is W wt % with gluconate, is attributed to the possible weak complexes formed with Ni and W, therefore making it more difficult to reduce.

<table>
<thead>
<tr>
<th>c</th>
<th>(-)</th>
<th>(-)</th>
<th>(+)</th>
<th>17.3 ± 2.2</th>
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</thead>
<tbody>
<tr>
<td>ab</td>
<td>(+)</td>
<td>(+)</td>
<td>(-)</td>
<td>58.2 ± 1.0</td>
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<tr>
<td>ac</td>
<td>(+)</td>
<td>(-)</td>
<td>(+)</td>
<td>26.7 ± 3.9</td>
</tr>
<tr>
<td>bc</td>
<td>(-)</td>
<td>(+)</td>
<td>(+)</td>
<td>29.3 ± 6.5</td>
</tr>
<tr>
<td>abc</td>
<td>(+)</td>
<td>(+)</td>
<td>(+)</td>
<td>47.9 ± 14</td>
</tr>
</tbody>
</table>
Figure 4. Effects of the three factors: pH, boric acid concentration and gluconate concentration on W wt%.
The added advantage of factorial design approach unlike the traditional research methods is examining the “combined effects” of the factors and their influence on a desired outcome. Figure 5 shows the combined effect of the factors on W wt %. Increasing both pH and concentration of boric acid had a minor negative effect on the W wt %. The combined effect of pH or concentration of boric acid with sodium gluconate resulted in a negative influence on W wt %, resulting from a drop in the W wt% in the deposit.

![Figure 5. Combined effects influencing wt% W.](image)

In our next phase of experiments, since sodium gluconate had a minor effect on the W wt%, we replaced sodium gluconate with temperature and examined its effect on W wt%. Similar electrode setup and deposition conditions were used as previously stated.
The only experiments added to the previous set of data were – (c, ac, bc and abc), where c= electrolyte temperature. The low (-) value of temperature was room temperature at 22°C and the high value (+) was maintained at 60°C. Each experiment was replicated three times. Table 9 shows the effect of three factors on the deposit outcome (W wt%).

Table 9. A $2^3$ experimental design for operational parameters, pH, boric acid and temperature

<table>
<thead>
<tr>
<th>Experiment notation</th>
<th>A pH</th>
<th>B Boric acid</th>
<th>C Electrolyte temperature</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>a</td>
<td>(+)</td>
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<td>(-)</td>
</tr>
<tr>
<td>b</td>
<td>(-)</td>
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<tr>
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<td>(-)</td>
<td>(-)</td>
<td>(+)</td>
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<tr>
<td>ab</td>
<td>(+)</td>
<td>(+)</td>
<td>(-)</td>
</tr>
<tr>
<td>ac</td>
<td>(+)</td>
<td>(-)</td>
<td>(+)</td>
</tr>
<tr>
<td>bc</td>
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<td>(+)</td>
<td>(+)</td>
</tr>
<tr>
<td>abc</td>
<td>(+)</td>
<td>(+)</td>
<td>(+)</td>
</tr>
</tbody>
</table>

Table 10 shows the deposit pictures and optical images with their corresponding W wt % and thickness, for the case where only temperature has been increased to 60 °C, measured using the X-ray fluorescence, to assess the deposition rate. The deposits obtained with boric acid were relatively brighter compared to Ni-W deposits from non-boric acid electrolytes.
Table 10. Summary of the factorial design experiments, deposit photographs, wt% W and deposit thickness

<table>
<thead>
<tr>
<th>Variables</th>
<th>Deposit Images</th>
<th>Optical images (50X)</th>
<th>W wt%</th>
<th>Deposit thickness (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment notation</td>
<td>A pH</td>
<td>B Boric acid</td>
<td>C Electrolyte temperature</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>(-)</td>
<td>(-)</td>
<td>(+)</td>
<td>![Deposit Image]</td>
</tr>
<tr>
<td>ac</td>
<td>(+)</td>
<td>(-)</td>
<td>(+)</td>
<td>![Deposit Image]</td>
</tr>
<tr>
<td>bc</td>
<td>(-)</td>
<td>(+)</td>
<td>(+)</td>
<td>![Deposit Image]</td>
</tr>
<tr>
<td>abc</td>
<td>(+)</td>
<td>(+)</td>
<td>(+)</td>
<td>![Deposit Image]</td>
</tr>
</tbody>
</table>

Figure 6 and Figure 7 show the effect of the three parameters: pH, boric acid concentration and temperature on W wt % and deposition rate respectively. Error! Reference source not found., shows that pH has the strongest influence on the W wt% followed by concentration of boric acid and temperature. The increase in Wt % of W could be attributed to the different tungstate ion species present in the electrolyte. Also, the Ni species present in the electrolyte also varies with pH which could have an impact on the deposition rate of W species itself. Error! Reference source not found. shows that temperature has the highest influence on deposit thickness, followed by pH and
concentration of boric acid. The increased thickness observed with increase in electrolyte pH could be due to higher current efficiency, while the increased deposition rate at high temperature could be explained by the increase in metal partial current densities. Although, the actual values on the W wt% or deposit thickness is not the main goal, but rather the effect of the parameters on the outcome is useful in designing experiments more effectively.

![Figure 6](image.png)

**Figure 6.** Influence of pH, boric acid and temperature on W wt%. 

12
10
8
6
4
2
0

Effect on W wt %

pH
Boric Acid
Temperature

Factors
Figure 7. Influence of pH, boric acid and temperature on deposition rate.

Figure 8 and Figure 9 shows the interaction effects of pH, boric acid and temperature on W wt % and deposit thickness respectively, that are at times tough to assess using traditional experimental procedures. As seen from Figure 8 even though boric acid and temperature individually have a positive effect on the W wt% in the deposit, their combined effect is not necessarily an additive effect as observed. Similarly is the case for all the factors ( pH-boric acid, pH –temperature), while the combined effect of all three factor has a positive influence on the W wt% in the deposit. Figure 9, shows the interaction effect of all the factors on the deposition rate. The combined effect of pH and boric acid has a positive influence on deposit thickness; this could be explained by the fact that the overall current efficiency of is higher, probably due to the
increased nickel deposition rate and due to the reduction of the $H^+$ ion concentration in the electrolyte, along with the combined buffering action of boric acid. The combined effect of pH-temp also has a positive influence on deposition rate. This could be attributed to the increase in metal partial current density compared to the side reaction rate (not examined here). The combined effect of boric acid and temperature seems to have no significant effect on the deposition rate, however, this effect could not be explained at this point without further analysis.

Figure 8. Interactions effects of the factors on W wt%.
The influence of temperature is compared in Figure 10 and Figure 11, where two deposits, one at the low temperature (RT, 22-25°C) and the other at the high temperature (60°C) are presented when deposited with boric acid in the electrolyte and at a pH of 8. The SEMs are reported at two different magnifications 700 X (Figure 9) and 35,000 X Figure 11. At the lowest magnification, cracks and large pits are clearly evident, likely the result of hydrogen embrittlement from the hydrogen evolution side reaction. There is a higher density of cracks at the lower temperature (Figure 10 (a)) than at the higher one (Figure 10 (b)). Interestingly, there are multiscale pits evident at higher magnification Figure 11. At low temperature the surface seems to have qualitatively larger pits (~200
nm, Figure 11(a)), and at the higher temperature, there are more numerous smaller pits with a large variation of size (~20-100 nm, (Figure 11 (b)). Note the whitish region surrounding the large pits. The white areas are due to the charging effect in the SEM and may be reflective of the less conductive hydroxide species being formed, owing to local pH changes. The morphology in the metallic regions looks different at low and high temperature. Both have a nodular-like appearance but they are smaller at low temperature than at the high temperature. This feature may be a signature of the grain size, but morphology in electrodeposition does not always indicate grain size.

![Figure 10](image1.png)

**Figure 10.** SEM images at 700× magnification of Ni-W deposits at (a) room temperature and (b) 60 ºC.

![Figure 11](image2.png)

**Figure 11.** SEM images at 35,000× magnification of Ni-W deposits at (a) room temperature and (b) 60 ºC.

Figure 12 and Figure 13 compare two deposits fabricated without the presence of boric acid in the electrolyte and with boric acid in the electrolyte at 60°C and at low
(Figure 12) and high (Figure 13) magnifications. There are about the same number of micro-cracks in the deposits, without (Figure 12 (a)) compared to when there is no boric acid in the electrolyte (Figure 12 (b)), but one significant difference is that there is a more uniform morphology when the boric acid is present. It is known that boric acid can help to buffer the surface, so the change in morphology may be related to local pH changes. Figure 13 shows a higher magnification of these deposits, again showing the nano-scale pits, but also showing small crystallites on the sample without boric acid (Figure 13(a)). These small features have a brighter contrast and suggest a difference in composition with elements that would make that region less conductive, such as boron or hydroxide compounds.

Figure 12. SEM images at 700× magnification of Ni-W deposits at 60 °C (a) without boric acid and (b) with boric acid.

Figure 13. SEM images 35,000× magnification of Ni-W deposits at 60 °C, (a) without and (b) with boric acid.
Using a factorial design approach, the effect of pH, boric acid, sodium gluconate, thiourea concentration and electrolyte temperature on W wt % and deposit thickness was examined. A quick assessment from these experiments indicated that while pH was determined crucial to increase the W wt% in the deposit, increased electrolyte temperature was beneficial to improve current efficiency. The advantage of employing a factorial design approach was highlighted by the assessment of the combined effect of the parameters on W wt % and deposit thickness. Although individually, the variables showed a positive effect on W wt%, the combined effect of either two variables did not significantly improve the W wt % in the alloy. Furthermore only, pH-boric acid and pH-temperature combination showed to improve the deposition rate of the alloy. Although the presence of boric acid did not seem to improve the W wt % or the deposit thickness, from the SEM analysis of the deposits obtained at pH 8, its presence in the electrolyte proved to be beneficial to obtain deposits with uniform morphology and composition. Increased electrolyte temperature was also beneficial in reducing the number of cracks in the deposit.

The effect of thiourea on Ni-W deposition was also examined using a factorial design approach and its effect on the W wt %. The electrolyte concentration is similar to the one described in
Table 1, without sodium gluconate. A higher concentration of thiourea 0.650 M was examined initially as the “high” value, however, the Ni-W deposit was non-metallic and powdery in appearance, and, the electrolyte was very unstable due to decomposition of thiourea during deposition, hence a lower concentration of thiourea 0.325 M was selected as the high value for the factorial design.

Table 11 show the deposit and optical images an along with the W wt% in the Ni-W alloy with the addition of thiourea to the electrolyte. A few observations that were clearly evident, from these experiments, is that low pH electrolyte, in this case pH 2, was beneficial to obtain metallic deposits under the applied deposition conditions, compared to the deposits obtained from a pH 8 electrolyte, containing thiourea. Furthermore, the electrolyte at pH 2 was relatively stable and no decomposition of thiourea was observed during deposition unlike the pH 8 electrolyte. The W wt% was higher from a pH 2 electrolyte compared to pH 8, this could be attributed to the presence of different tungstate species present in the electrolyte. The addition of boric acid had different effects depending on the pH of the electrolyte, in the case of pH 2 electrolyte with thiourea, an increase in W wt % was observed, as opposed to a decrease in W wt % in pH 8. Furthermore, the deposits at pH 8 are non-metallic in appearance, which is not desirable, which could be due to the high inclusion of S in the deposit, forming a rich Ni-S alloy.

Table 11. Summary of the factorial design experiments, deposit photographs, wt% W and deposit thickness

<table>
<thead>
<tr>
<th>Variables</th>
<th>A pH</th>
<th>B Boric</th>
<th>C Thiourea</th>
<th>Deposit Images</th>
<th>Optical images</th>
<th>W wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment notation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>------</td>
<td>-------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>(-)</td>
<td>(+)</td>
<td>6.8 ± 3.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ac</td>
<td>(+)</td>
<td>(-)</td>
<td>11.8 ± 4.6</td>
<td></td>
<td></td>
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<td>bc</td>
<td>(-)</td>
<td>(+)</td>
<td>4.6 ± 2.8</td>
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<td></td>
</tr>
<tr>
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<td>(+)</td>
<td>(+)</td>
<td>3.3 ± 1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 14 and *Error! Reference source not found.* show the effect of the three parameters: pH, boric acid concentration and thiourea and their interaction effects on W wt % respectively. *Error! Reference source not found.*, shows that pH has the strongest influence on the W wt% followed by concentration of boric acid and thiourea. The decrease in W wt % could be attributed to either the possible adsorption of thiourea onto the electrode surface, inhibiting W from reducing at the surface, or since thiourea also forms a complex with Ni, including the Ni-Cit reduction pathway could increase Ni wt % in the deposit. From these experiments it was evident that the addition of thiourea was not beneficial to increase the W wt % in the deposit. Only the interaction effect of all three factors a positive effect on the W wt % in the deposit.
Figure 14. Influence of pH, boric acid and thiourea on W wt %.
4.2 **Effect of Additives on Ni and Ni-W Electrodeposition**

As mentioned in section 2.2.1, the presence of BD, influences the surface appearance and is also known to improve corrosion resistance of the deposit. In this section, the influence of BD on the deposition behavior of Ni and Ni-W alloys is presented.

4.2.1 **Effect of 2 Butyne-1,4-diol (BD) on Ni Electrodeposition at pH 2**

The electrodeposition behavior of Ni was examined in the presence of BD similar to the concentrations mentioned in Table 2, without the presence of boric acid in the
electrolyte to begin with. Once this was established, the influence of BD in the presence of boric acid followed by increased electrolyte temperature was examined. The electrolyte pH was varied between 2 and 8. A conventional Hull cell in the configuration setup in Figure 1(a) which is expected to result in a current distribution was used for these set of experiments, to examine the effect of current density on deposit composition and thickness. The air agitation rate was maintained at 3 L/min and the average applied current density was 50 mA/cm² for duration of 30 min. Figure 16 shows the polarization curves of Ni with varying concentrations of BD. A decrease in the current density towards negative potentials occurs with BD addition to the electrolyte at low values of current density. A much larger effect is seen for the 5 mM case. This inhibition effect of BD is consistent with previous literature reports [83]–[85].
Figure 16. Polarization curves for Ni electrolyte with variable amounts of BD.
Figure 17 shows the photographs of the Hull cell Ni deposits – (a) without BD, (b) 1mM BD, (c) 2.5 mM BD and (d) 5 mM BD. The chosen applied current density captures the low current density region where only the side reaction occurs due to proton reduction, a mid-range region where the nickel appears dull, and then a higher current density region where the deposit is bright metallic. The photographs show that the air agitation used in the Hull cell reflects streaks from the agitation on the deposit only when BD is present, this could be due to the mass transport behavior of BD on the metal deposition. These streaks are absent when BD is not present. In addition, an increase in BD concentration, transitions the deposit appearance to a more bright surface, as expected, since BD is known as a representative class II brightening agent [86].
In order to estimate the local applied current density along the cathode length, a primary current distribution was assumed (This current distribution is the estimate commonly provided by manufacturers of the Hull cells.). To evaluate the validity of using this approach, the Wagner number was determined at the average current density employed in the Hull cell:

\[ Wa = \frac{\partial E/\partial i}{L/\kappa} \]  

(1)
where $\kappa$ is the conductivity and $L$ is the electrode length. The derivative $(\partial E/\partial i)$ can be experimentally determined from the slopes of the polarization curves. The corresponding Wagner numbers under these conditions are: 0.015 (No BD), 0.0125 (1 mM BD) and 0.0075 (2.5 mM and 5 mM) respectively which are all $<<1$. Therefore, the total current density distribution along the Hull cell configuration is governed largely by an ohmic controlled resistance, and a primary current distribution is a reasonable approximation of the local current density. Once we have established we have primary current distribution along the length of the cathode, we can then correlate each point on the cathode to an approximate applied current density at that location using a Hull cell current distribution equation:

$$\frac{i(z)}{i_{avg}} = \frac{z^{1.273}}{1 - z^{0.359}} (1.733 - 0.763z)[1 + 0.065(z - z^2)]$$

where $z$ is the dimensionless length along the length of the cathode.

The thickness results in Error! Reference source not found. correlate the position along the electrode with an estimated current density, assuming a primary current distribution. The thickness increases with the estimated applied current density for all BD electrolytes and there is little difference at the low current density region. At higher current density, there is a substantial change in thickness with BD, with a thinner deposit resulting with additions of BD in the electrolyte.
Figure 18. Deposit thickness across the Hull cell correlated with an estimated current density for different amounts of BD in the electrolyte.

Using Faraday’s law,

\[ i_j = \frac{LX_jnF}{\sum_j(\frac{x_j}{p_j})M.wt_j\times t} \]

the partial current densities were determined from the deposit thicknesses that were measured from the XRF, scanning locally across the electrode surface and assuming that the density of nickel was its bulk value. Figure 19 uses the polarization curves from Figure 16 to transform the current density to an estimated applied potential, more useful for comparing the effect of the driving force of the reaction.
Figure 19. Nickel partial current density for different amounts of BD in the electrolyte.

Figure 20 shows the effect of BD on the side reaction partial current density. As the BD concentration in the electrolyte increases there is a decrease in the side reaction partial current density, and this decrease is the reduction in the total current density observed in the polarization curves in Figure 16. However, even though the side reaction partial current density decreased, the reduction in the thickness of the deposit is attributed to the reduction in the Ni partial current density alone.
4.2.2 Effect of 2 Butyne-1,4-diol (BD) on Ni-W Electrodeposition at pH 2

The electrodeposition behavior of Ni with tungsten was examined in the presence of BD. The electrolyte used in this case was the same as the nickel electrolyte with an addition of 0.15 M sodium tungstate. A conventional Hull cell in the configuration setup in Figure 1 (a) was used for these set of experiments, to examine the effect of current density on deposit composition and thickness. The air agitation rate was 3 L/min and the average applied current density was 50 mA/cm$^2$ for duration of 30 min, resulting in a distribution of current density. The pH was maintained at a value of 2 or 8.

Error! Reference source not found. shows the polarization curves for Ni-W deposition with varying amounts of BD. A shift of the polarization curves toward more
positive potentials was observed in the Ni-W electrolyte as the BD concentration increased. This unusual polarization behavior is opposite to what is observed in a nickel electrolyte during nickel electrodeposition.

Figure 21. Polarization curves for Ni-W electrolyte with variable amounts of BD.

Srinivasan and Bapu [83] showed an inhibiting effect of the total current density with an increase in BD concentration in a nickel-containing electrolyte. In addition, the same electrolyte with only nickel ions present, Figure 16, is consistent with the literature and shows an opposite trend to Error! Reference source not found., when tungstate is added to the electrolyte.
Figure 22 compares the polarization curves for Ni and Ni-W (a) without BD and (b) 5 mM BD, which are re-plotted from Figure 16 and Error! Reference source not found. for clarity. The polarization behavior of Ni and Ni-W electrolytes with (a) No BD and (b) 5 mM BD are significantly different. When there is no BD present the Ni-W polarization curve lies to more negative potentials, while when BD is present the Ni-W curve is more positive. Thus, the introduction of tungstate to the electrolyte is the reason behind this
unusual behavior.

![Graph (a)](image1)

![Graph (b)](image2)
Figure 22. Polarization curves for Ni and Ni-W electrolyte with (a) No BD and (b) 5 mM BD.

Figure 23 (a-d) shows images of the Ni-W deposit obtained on the Hull cell with varying concentrations of BD. The deposits without BD appear to be light gray in color with a reflective surface. The deposit appearance tends to increase in brightness at higher current densities with increasing BD concentration. Furthermore, no deposition occurs at lower current densities with increasing BD concentration. At the highest BD concentration examined, (5 mM, Figure 23 (d)), little or no deposit was obtained over a large deposition range. Also, there was an interesting pattern seen in the deposits produced under air agitation. In areas where the air bubbles rose, no deposit was seen. This could indicate that an increase in BD transport to the electrode surface had an inhibiting effect on the alloy deposition.
Figure 23. Images of Ni-W deposit from low to high current density (right to left) with varying amounts of BD at an average current density of -50 mA/cm²: (a) No BD, (b) 1 mM BD, (c) 2.5 mM BD and (d) 5 mM BD.

In order to investigate the source of the polarization shift in the Ni-W electrolyte, the partial current densities were determined. The partial current densities can help to indicate if the observed increase in the total current density at a given potential with BD is due to an increase in the metal deposition rate or due to an increase in the side reaction. In order to determine the partial current densities of the overall reactions, both composition and mass measurements are needed over a range of current densities.
The deposit composition obtained with XRF along the length of the Hull cell is presented in Figure 24 as a function of estimated current density assuming primary current distribution. In all cases, the alloys are nickel-rich. In Figure 24 (a), an increase in nickel content is observed in the alloys with an increase in the amount of BD present in the electrolyte. The composition in this range is relatively unaffected by the total current density. An inverse behavior is seen in the case of tungsten (Figure 24 (b)), with a subsequent reduction in the amount of tungsten with BD.
Figure 24. Composition as a function of current density for (a) Ni wt% and (b) W wt%.

Figure 25 shows the variation in thickness with and without varying concentrations of BD in the electrolyte. The deposit thickness increased with increasing current density in all the examined cases. In the case where BD was introduced into the electrolyte, there was a decrease in the deposit thickness.
Figure 25. Ni-W deposit thickness with varying amounts of BD.

In Figure 26 (a-b) a comparison is made between the partial current densities for nickel, and tungsten with varying concentrations of BD calculated from Faraday’s law. The x-axis in Figure 26 is the working electrode potential determined by interpolating the potential from the polarization curve in Figure 21, using the values of the estimated local current density along the length of the Hull cell cathode. From Figure 26 (a), there is a shift in the nickel deposition potential to a more positive value. However, comparably, there is less change of the tungsten partial current density with potential (Figure 26 (b)). Thus, the shift in the nickel reduction rate is what accounts for more nickel in the deposit.
Figure 26. Effect of BD concentration on (a) nickel, and (b) tungsten partial current densities.
Figure 27 shows the partial current density for the side reaction. There is a shift in potential with the side reaction, which is a result of the hydrogen evolution reaction. The biggest change in the side reaction is when BD is introduced, but then additional amounts of BD introduced have very small effects on the side reaction rate. Thus, the observed thickness decrease with BD present in the electrolyte (Figure 25) is due to the increase in the side reaction rate.

**Figure 27. Effect of BD concentration on side reaction partial current densities.**

The Tafel slopes for each of the reactions were estimated within the potential range of -0.6 and -1.1 V, which is a kinetically-controlled region for nickel and tungsten deposition. The values are plotted in
Figure 28 for (a) Ni and (b) W and listed in Table 12. The presence of BD in the electrolyte seems to enhance the nickel deposition by shifting the deposition to more positive values with increasing concentrations of BD, however it does not significantly affect the Tafel slopes and hence the kinetic mechanism may be the same.
Figure 28. Tafel slope kinetics for W deposition with varying concentrations of BD for (a) Ni and (b) W.

Table 12. Tafel slopes (mV/dec) of Ni-W alloys with varying concentrations of BD

<table>
<thead>
<tr>
<th>BD concentration</th>
<th>Nickel</th>
<th>Tungsten</th>
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</thead>
<tbody>
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<td>163</td>
</tr>
<tr>
<td>1</td>
<td>105</td>
<td>125</td>
</tr>
<tr>
<td>2.5</td>
<td>94</td>
<td>105</td>
</tr>
<tr>
<td>5</td>
<td>122</td>
<td>120</td>
</tr>
</tbody>
</table>
4.2.3 Effect of 2 Butyne-1, 4-diol (BD) on Ni-W Electrodeposition at pH 8

In an effort to improve current efficiency and hence deposit thickness, we examined the effect of BD on Ni-W electrodeposition at a higher pH. A higher pH helps in improving the current efficiency, by eliminating the side reaction \(2H^+ + 2e^- \rightarrow H_2\) by lowering the concentration of \(H^+\) ions in the electrolyte. Also, Ni-W is typically electrodeposited at high pH with a complexing agent for nickel ions to prevent its precipitation. The electrolyte concentrations and deposition conditions used are similar to the one used is section 4.1.2, with the only exception that the electrolyte is now maintained at pH 8.

Figure 29 shows polarization curves of the Ni-W electrolyte at pH 8 with different amounts of BD. Again there is a depolarizing effect, a shift in the curves in a positive direction, with the addition of BD. Recall in Figure 21 that, at pH 2, a similar behavior was observed for the same Ni-W polarization.
Figure 29. Polarization curves at pH 8 in the Ni-W electrolyte surface.

Figure 30 shows the images of the Ni-W deposits from a pH 8 electrolyte. The deposition occurs along the entire length of the Hull cell with increasing concentrations of BD, unlike the deposition from pH 2. The deposits also appear reflective relative to the deposits obtained from pH 2 electrolyte. The region where the air flow occurs appear to be brighter than the regions in between, indicating the mass transport effects of BD towards the electrode surface towards Ni-W deposition.
Figure 30. Ni-W deposit along a Hull cell with (a) no BD, (b) 1 mM BD, (c) 2.5 mM BD and (c) (d) 5 mM BD, at pH 8.

Figure 31 (a) and (b) show the deposit composition as a function of current density with increasing concentrations of BD in the electrolyte. An increase in BD tends to increase the amount of Ni in the deposit in the low to mid current density region, which is similar to that observed in the pH 2 electrolytes, followed by a decrease at the higher applied current densities.
Figure 31. Deposit composition at the estimated applied current densities, pH 8 for (a) nickel and (b) tungsten.

The deposit thickness is presented in Figure 32. An addition of 1 mM BD produces no substantial change on the deposit thickness, but at 2.5 and 5 mM BD, a
significant decrease in the deposit thickness is observed. In general, the deposit thickness for the same time of deposition is much lower than even pH 2 when BD is added to the electrolyte.

![Diagram showing deposit thickness across the Hull cell correlated with estimated current density for different amounts of BD in the electrolyte.](image)

**Figure 32. Deposit thickness across the Hull cell correlated with an estimated current density for different amounts of BD in the electrolyte.**

The partial current densities (Figure 33) show a substantial decrease in both the nickel and tungsten partial current densities with BD. Unlike the pH 2 case, the increase in the nickel deposit content is due to the relatively larger decrease in the tungsten partial current density as compared to the nickel partial current density. This behavior is consistent with the reported action of BD on nickel reduction, leading to a decrease of the nickel partial current density with BD concentration in the electrolyte.
Figure 33. Partial current densities of nickel and tungsten with various amounts of BD, at pH 8 for (a) Ni and (b) W.
Figure 34 shows the side reaction partial current density for pH 8 with increasing concentrations of BD. The side reaction partial current density increases with increasing BD concentration, and the increase observed in the total current density from the polarization curves in Figure 29 is due to the enhanced side reaction alone, since both the metal partial current densities decrease with BD.

![Graph showing the side reaction partial current density with increasing BD concentrations at pH 8.](image)

**Figure 34. Side reaction partial current density with increasing BD concentrations at pH 8.**

The partial current density behavior for Ni and W is very different with the change in pH of the electrolyte. Figure 35 (a) shows re-plotted data from Figure 26 (a) Figure 33 (a) comparing Ni partial current density for 5 mM BD concentration at pH 2 and pH 8 respectively. Similarly, Figure 35 (b) shows re-plotted date from Figure 26 (b) and Figure 33 (b) comparing W partial current density for 5 mM BD concentration at pH 2 and pH 8.
The behavior for Ni in Figure 35 (a) and for W in Figure 35 (b) shows that the current-potential behavior has a larger slope at pH 2 compared to 8, however, for the current density applied for pH 2, the potential does not extend to the examined potential for the pH 8 electrolyte and compressive conclusion cannot be made at this point. The difference in behavior could be attributed to the different Ni and W ionic species present in the electrolyte, having different deposition rates.
Figure 35. Different behavior observed at two different pH values for (a) Ni and (b) W.

Table 13 summarizes the dominating metal complex species that are at equilibrium in the bulk electrolyte. The assumption is that nickel and tungstate completely dissociate to form Ni$^{2+}$ and WO$_4^{2-}$ and complex with the citrate ligand (Cit= C$_6$H$_5$O$_7$).

Table 13. A selection of the most significant Ni- and W-citrate species and equilibria

<table>
<thead>
<tr>
<th>Species</th>
<th>Equations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCit$^-$</td>
<td>$\frac{C_{NiCit^-}}{C_{Ni^{2+}}C_{Cit^{3-}}}$ = $10^{5.35}$</td>
<td>[87]</td>
</tr>
<tr>
<td>NiHCit</td>
<td>$\frac{C_{NiHCit}}{C_{Ni^{2+}}C_{Cit^{3-}}-C_{H^+}}$ = $10^{9.13}$</td>
<td>[87]</td>
</tr>
<tr>
<td>NiCit$_2^{4-}$</td>
<td>$\frac{C_{NiCit_2^{4-}}}{C_{Ni^{2+}}C_{Cit^{4-}}}$ = $10^{8.11}$</td>
<td>[87]</td>
</tr>
</tbody>
</table>
Together with Table 13 and the mass balance equations for nickel, tungstate and citrate species, Figure 36 is generated, comparing graphically as to what species dominate at the two different pH values. The difference in deposition behavior and the resulting composition in the deposit are attributed to the different species present at different pH values. Different Ni-Cit and WO₄-Cit complexes could possess different reduction rates that can be sensitive to adsorbed intermediates.
4.2.4 Effect of Boric acid on Ni-W Deposition with 2 Butyne-1,4 diol (5 mM)

From the previous factorial design experiments it was evident that boric acid and temperature have a huge effect on the deposit composition and thickness. Deposits with boric acid tend to lead to more uniform deposition due to a pH buffering effect of boric acid. In order to improve the metal deposition rates and hence the current efficiency, the effect of boric acid on Ni-W alloys containing BD was examined. Figure 37 shows the effect of boric acid concentration in the electrolyte on the deposition behavior of Ni-W alloys. With increasing concentrations of boric acid, there is an inhibitory effect on the total current in the range of -0.6 to -1.2 V at low current densities. Above a cathodic current density of 50 mA/cm² the total current density doesn’t follow a trend with the
addition of boric acid. There is a sharp increase in current density for the 0.5 M boric acid case at a potential of about -1.1 V, indicative of the exponential increase in water reduction, while the current density for the 1 M boric acid case shows a rise in current density occurs at more negative potential values. A closer look at the deposit composition, thickness and the determination of partial current densities enables the understanding of whether the metal or side reaction partial current density is affected by the boric acid electrolyte concentration.

Figure 37. Polarization curves for Ni-W with 5 mM BD for varying concentrations of boric acid.

Figure 38 (a), (b) and (c) shows the Ni-W deposits with BD, for increasing amounts of boric acid in the electrolyte. All the deposits appear reflective, and the
addition of boric acid is beneficial in eliminating the visual air patterns, which lead to more uniform deposits.

Figure 38. Ni-W deposit images from low to high current density (right to left) with 5 mM BD for (a) No boric acid, (b) 0.5 M boric acid and (c) 1 M boric acid.

The effect of boric acid concentration on thickness is shown in Figure 39. Increasing the boric acid concentration to 0.5 M, increased the thickness of the deposit in the mid current density range, before leveling off at higher applied current densities. Further increase in boric acid concentration to 1 M, resulted in a minor increase in deposit thickness, which also levels off at higher current densities.
Figure 39. Effect of boric acid concentration on deposit thickness.

The alloy composition of the deposits with varying concentrations of boric acid is shown in Figure 40 for (a) Ni wt% and (b) W wt %. The addition of 0.5 M boric acid increased the W wt % in the alloy drastically in the low current density region, and levels off at higher applied current densities. Further addition of boric acid to 1 M, does not significantly affect the deposit composition and remains the same as the 0.5 M boric acid case.
Figure 40. Deposit composition of the alloy with increasing concentrations of boric acid in the electrolyte.
Figure 41 shows the partial current densities for (a) Ni and (b) W when the concentration of boric acid is increased. In both cases there is a substantial enhancement in their partial current densities. There is also a small shift in the metal deposition potential to more negative values with increasing boric acid concentration as observed in Figure 41 (a) and (b). The reason for the increase in the deposit composition of W wt % is thus due to greater increase in the W partial current density than the Ni partial current density.
Figure 41. Partial current densities with varying concentrations of boric acid for (a) Ni and (b) W.

From the side reaction partial current density shown in Figure 42, the addition of boric acid shifts the side reaction partial current to more negative potentials. The increase in metal deposition rates in the presence of boric acid may be associated with its surface adsorption behavior. Boric acid can act to inhibit other reactions through a decrease of active sites on the electrode surface and preferentially retards the hydrogen evolution rate (HER). This behavior is supported by several other publications [89]–[91]. Kareas and Hepel [89] examined the electrodeposition of Ni-Zn alloys in the presence of boric acid and found that, boric acid interferes with the nucleation process and reduces HER in the presence of Ni-enriched phases. They attributed adsorption of boric acid to the observed changes in surface morphology. This is beneficial in improving the overall current efficiency as shown in Figure 43. In the absence of boric acid a higher side reaction partial current density is observed, which results in ~2 % current efficiency. Upon
addition of 0.5 M boric acid, the current efficiency increases to ~ 10 % in the same
applied potential range, and decreases with increase in potential, further increase in boric
acid concentration does not increase the current efficiency further.

Figure 42. Effect of boric acid concentration on the side reaction partial current
density.
Figure 43. Effect of boric acid concentration on overall current efficiency.

4.2.5 Effect of Temperature

To further improve the overall current efficiency of the electrolyte, Ni-W deposition with BD with 0.5 M boric acid was examined at 60 °C. Increasing the electrolyte temperature is supported by the fact that, a lower activation barrier is required for a reaction to occur, thereby increasing the reaction rate of a specific reaction. Figure 44 shows the effect on increasing the electrolyte temperature on deposition behavior for a Ni-W electrolyte with 5mM BD and 0.5 M boric acid. An increase in current density is observed with increase in temperature. , (a) Ni, (b) W and (c) side reaction shows that an increase in electrolyte temperature to 60 °C, increased the metal deposition rates and substantially decreased the side reaction partial current density.
From the composition analysis, no significant change in the alloy composition is observed with increase in electrolyte temperature, as shown in Figure 45 (a) Ni wt %, and (b) W wt %, which could be beneficial since similar alloy composition would retain the alloy properties desirable. Thereby an increase in the thickness of the deposit and hence the current efficiency is the observed effect from increased electrolyte temperature.
Figure 45. Composition of the alloy with increase in electrolyte temperature (a) Ni wt % and (b) W wt %.
Figure 46 (a) Ni, (b) W and (c) side reaction, shows that an increase in electrolyte temperature to 60 °C increased the metal deposition rates and substantially decreased the side reaction partial current density.
Figure 46. Effect of temperature on partial current density, 0.5 M boric acid for (a) Ni, (b) W and (c) side reaction.
The effect of increased electrolyte temperature also shifted and decreased the side reaction partial current density to more cathodic potentials. This resulted in an overall increase in current efficiency from ~10 % to ~ 25 % as shown in Figure 47.

Figure 47. Effect of temperature on the overall current efficiency, 0.5 M boric acid.

The work presented above was submitted to the National Association for Surface Finishing for publication and are cited below:

4.2.6 Effect of Thiourea Concentration on Ni-W Electrodeposition

The factorial analysis indicated that electrodeposition of Ni-W alloys from a pH 2 electrolyte resulted in reflective metallic deposits compared to deposits from a pH 8 electrolyte, despite the expected increase in the side reaction due to proton reduction. In this section, the thiourea concentration suitable for Ni-W alloy deposition was determined for a pH 2 electrolyte without boric acid. The effect of thiourea concentration on Ni-W deposition from a citrate electrolyte on deposit quality, composition and thickness is examined here. The Ni-W citrate electrolyte contained 0.5 M nickel sulfate, 0.15 M sodium tungstate, 0.5 M sodium citrate and varying concentrations of thiourea (0.065 M, 0.325 M and 0.650 M) at pH 2. A high concentration of nickel and citrate was examined in this set of experiment, which would be useful for further experiments examined in section 4.4. The amount of sulfur content in the deposit is also analyzed. A conventional Hull cell was used to examine the effect of current distribution on the deposit composition and quality.

Figure 48 shows the Ni-W deposits obtained from a conventional Hull cell, with air agitation (3 L/min). The average applied current density is 10 mA/cm², with copper as the substrate. The composition and thickness of the deposit was measured using X-ray fluorescence.

When thiourea was not present, the deposit appeared light grey in color with a reflective surface. The deposit appearance turned darker and rougher with increasing concentrations of thiourea. In Figure 48 (a) without thiourea, no deposit was obtained at the lower current densities, but with the addition of even small amounts of thiourea, a deposit was obtained at lower current densities (Figure 48(b-d)), indicating a change in
the current-potential behavior that maybe attributed due to a change in reacting species, such as a Ni-thiourea complex.

![Figure 48. Ni-W deposition on a Hull cell, low CD to high CD (L-R) with: (a) no thiourea, (b) 0.065M thiourea (c) 0.325M thiourea and (d) 0.625M thiourea.](image)

The composition analysis of the deposits with varying amounts of thiourea is shown in Figure 49. The curves for nickel (Figure 49 (a)), tungsten (Figure 49 (b)) and sulfur (Figure 49 (c)) show the effect of current density on the composition, with increasing wt % for Ni with increasing current density and the opposite effect for S and W wt %. However, with increasing concentration of thiourea, an increase in S wt % was observed at the expense of Ni in the deposit. An interesting observation is the reduction in the tungsten content in the deposit. This may be attributed to the loss of the free Ni$^{2+}$ species that helps to induced tungsten codeposition and/or the adsorption of thiourea.
Figure 49. Composition distribution along the Hull cell length for (a) Ni wt% (b) W wt% and (c) S wt%.

With a large amount of sulfur present in the deposit, it is possible that the nickel and tungsten deposits were not completely reduced. Thus the partial current density, which requires knowledge of the number of electrons transferred, was not determined. Tran et al. [92] reported on Ni-W-S films, where the metals have a valence of II and IV, respectively for Ni and W, that exhibit catalytic properties towards the hydrogen evolution reaction during water splitting. However, since a cathodic current density was used here, it is expected that the valence state of the metals may be less than II and IV, respectively for Ni and W. Whether the partially reduced Ni-W-S is a viable electrocatalyst is a subject for future work.

Furthermore, as mentioned earlier in Table 13, nickel forms stable complexes with citrate and thiourea, and using the stability constants of various Ni, W citrate complexes the dominant complex species present for the electrolyte in Table 2 was
determined, as presented in Figure 50. Three dominant species of nickel ions in the electrolyte are expected: an uncomplexed Ni$^{+2}$, a nickel-citrate complex NiHCit$_2$, and a nickel thiourea complex in the electrolyte. The largest nickel species is the one complexed with citrate, and the addition of thiourea does not significantly change that dominance. However, the role of the thiourea helps to complex the free, Ni$^{+2}$ ions to form the Ni-TU complex. Another interesting observation is the reduction in the tungsten content in the deposit. This may be attributed to the loss of the free Ni$^{+2}$ species that could help to induced tungsten codeposition and/or the adsorption of thiourea.

Figure 50. Distribution of free Ni$^{+2}$, NiHCit$_2$ and Ni-thiourea (Ni-TU) complex species for varying amounts of thiourea.

Figure 51 shows the effect of thiourea concentration on the deposit thickness. No significant increase in the deposit thickness is observed until the thiourea concentration is increased to 0.650 M with increasing current density before reaching a plateau. However, the deposits obtained at this concentration are expected to be nickel sulfide
films, consistent with the observations made by Mohanty et al. [59], where 40 mg/dm$^3$ of thiourea resulted in rough black Ni deposits.

![Figure 51. Deposit thickness as a function of thiourea concentration in the electrolyte.](image)

The work presented above was submitted to the National Association for Surface Finishing Surface Technology White Papers and are cited below:

4.3 **Electrodeposition of Ag-W alloys**

When thiourea addition is used as a brightener or leveler to Ni electrodeposition a small concentration is required. However, when silver ions are present, thiourea complexes with them, which has the added benefit of improved stability in electrolytes containing a mixture of metal ions. Figure 52 (a) and (b) show the electrolyte stability for a 5 mM Ag\(^{+}\) electrolyte with 65 mM thiourea and 200 mM thiourea at pH 2. From an experimental observation standpoint, a 1:4 ratio of \(\frac{[Ag^{+}]}{[TU]}\) is required to complex Ag and maintain electrolyte stability (clear solution).

![Figure 52](image1.png)

**Figure 52.** Electrolyte stability for 5 mM Ag\(^{+}\) with (a) 65 mM thiourea and (b) 200 mM thiourea.

### 4.3.1 Effect of W (VI) Concentration on Ag-W Electrodeposition

Figure 53 shows the polarization curves for different W (VI) concentrations with 5 mM Ag at a constant RCE rotation rate. The total current density in the polarization curves increases with an addition of the tungsten ion concentration in the electrolyte. The
large increase in the total current density at more negative applied potentials occurs at considerably more noble values with the presence of 30 mM tungsten ions compared to the case when only silver metal ions are present (Figure 53 (a) and (b)). A further increase in tungsten ion concentration to 75 mM (Figure 53(c)) increases the current density slightly and an increase to 150 mM (Figure 53(d)) of the tungsten ion concentration has no significant change at large negative potentials compared to the 75 mM case. Thus, higher tungsten ion concentration was not examined due to this limiting feature in the polarization curves. An apparent limiting current density region at 2.5 mA cm$^{-2}$ in the potential range of (-0.3 V to -0.55 V) is observed (in the inset of Figure 53), which may be attributed to the Ag, proton and oxygen diffusion limited current density. The increase in current density with potential is expected to be due to the additional tungsten reduction and the hydrogen evolution reaction from water. Examining the partial current densities through steady state analysis of the deposit composition and deposit thickness is used to help to deconvolute the different reactions reflected in these polarization curves.
Figure 53. Polarization curves for 5 mM Ag, 250 mM TU, and 285 mM Cit with (a) 0, (b) 30 mM, (c) 75 mM and (d) 150 mM tungsten ion electrolyte concentration at a scan rate of 10 mVs⁻¹ and 350 rpm.

Figure 54 shows the deposit composition of W in the Ag-W alloys, characterized by XRF at different applied current densities and sodium tungstate electrolyte concentrations. The composition is based on only the metallic elements. As the current density increased, the amount of tungsten content reached a limiting value of 2 wt % for the low concentration of 30 mM tungsten ions. A further increase to 75 mM and 150 mM tungsten ion concentration increased the W incorporated in the deposit with increasing current density. The highest amount of tungsten obtained was 18.2 wt % for 150 mM at
an applied current density of 320 mA/cm². Deposits obtained at higher current density were powdery and non-adherent and were therefore not further analyzed. A significant implication of this result is that the ratio of tungsten ions to silver ions are way above one, and larger amounts of W was codeposited unlike the study of Inberg et al. [24] but similar to the literature reports of Cu-W codeposition [78].

![Graph](image-url)

**Figure 54. Deposit composition of W in the alloy with increasing amounts of tungsten ion electrolyte concentration.**

In order to better understand the deposition behavior the partial current densities were determined by applying Faraday’s law using the measured composition, Figure 54 and the deposit thickness from the XRF. In Figure 55, the partial current densities for (a) Ag and (b) W is presented, assuming a one electron transfer for silver ions and six
electron transfer for tungsten ions. The measured resulting working electrode potentials were corrected for ohmic drop. The Ag partial current density remains constant with increasing current density and working electrode potential; this is expected since Ag is under diffusion limited control. Approximating the boundary layer using the Eisenberg correlation [93] the diffusion coefficient for the Ag complex, when tungsten was not present, was found to be $1.5 \times 10^{-5}$ cm$^2$ s$^{-1}$, which is comparable to an uncomplexed silver ion diffusion coefficient in water. With the addition of tungsten ions to the electrolyte there is considerable gas evolution at the electrode so the boundary layer thickness would be expected to be slightly smaller with an accompanying increase in the Ag limiting current density, which is observed in Figure 55 (a). The W partial current density increases with the applied potential, typical of kinetic control. An estimate of the limiting current densities for the three concentrations of tungsten ions are: 16, 40 and 80 mAcm$^{-2}$ for the corresponding concentrations of 30, 75 and 150 mM. Thus, the W partial current densities are indeed well below their possible limiting current densities. In the absence of silver ions no metallic film was observed. Thus, while other literature studies emphasize the concentration of the inducing ions, in this case silver, as a key parameter that dictates the ability to reduce tungsten ions, the results presented here, suggest otherwise. With a small amount of silver ions in the electrolyte compared to tungsten ions there is still an increase in the W deposit concentration, it is not limited by the low amount of silver.
Figure 55. Metal partial current densities with variable tungsten ion electrolyte concentration (a) Ag and (b) W.
The partial current density of the side reaction was deduced by the difference between the total current density and the sum of the metal current densities, shown in Figure 56. Clearly the increase in the total current density at large negative potentials in Figure 53 are due to the side reaction, as reflected in Figure 56, and predominately governed by the hydrogen evolution side reaction from water reduction. The addition of tungsten ions in the electrolyte accelerates the side reaction. There is a limiting feature, however, beyond 75 mM there is no further increase in the side reaction with more tungsten ions. Similarly, while there is a large increase in the W partial current density between 30 mM and 75 mM, Figure 55 (b), there is only a minor increase in the W partial current density from 75 mM and 150 mM. The results suggest that the side reaction is also coupled the W deposition rate.
Figure 56. Side reaction partial current densities with variable tungsten ion electrolyte concentration.

Table 14 lists the chemical equilibria equations used to generate this data, with TU and citrate ligands. At high thiourea concentration the dominate Ag ion species is complexed as AgTU₄ (3.1 mM) and AgTU₃ (1.9 mM) which remains unaffected with pH. Other Ag complex species (AgTU and AgTU₂) were also included in the calculation, but were not plotted here as their concentrations were negligible. The tungsten species has only one complexed species present in substantial concentrations, at pH 2, WO₄HCitH₃ species. With a large amount of side reaction, it is expected that the surface pH may rise. Thus, the larger amount of W in the deposit occurs with a higher amount of the side reaction and an expected change of species to the less protonated form.
Table 14. Reactions and Eqs used to generate euilibrium plot, Cit= C₆H₅O₇

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$WO_4^{2-} \ + \ H^+ \ + \ HCit^3- \ \rightarrow [WO_4HCitH]^4-$</td>
<td>$10^{10.2} = \frac{[WO_4HCit]^3^-}{[WO_4^{2-}][H^+][HCit^3-]}$</td>
</tr>
<tr>
<td>$WO_4^{2-} \ + \ 2H^+ \ + \ HCit^3- \ \rightarrow [WO_4HCitH_2]^3-$</td>
<td>$10^{17.03} = \frac{[WO_4HCitH_2]^3^-}{[WO_4^{2-}]^2[H^+]^2[HCit^3-]}$</td>
</tr>
<tr>
<td>$WO_4^{2-} \ + \ 3H^+ \ + \ HCit^3- \ \rightarrow [WO_4HCitH_3]^2-$</td>
<td>$10^{21.67} = \frac{[WO_4HCitH_3]^3^-}{[WO_4^{2-}]^3[H^+]^3[HCit^3-]}$</td>
</tr>
<tr>
<td>$Ag^+ \ + \ TU \ \rightarrow [AgTU]^+$</td>
<td>$10^{7.11} = \frac{[AgTU]}{[Ag^+]TU}$</td>
</tr>
<tr>
<td>$Ag^+ \ + \ 2TU \ \rightarrow [AgTU_2]^+$</td>
<td>$10^{10.61} = \frac{[AgTU_2]}{[Ag^+]TU^2}$</td>
</tr>
<tr>
<td>$Ag^+ \ + \ 3TU \ \rightarrow [AgTU_3]^+$</td>
<td>$10^{12.73} = \frac{[AgTU_3]}{[Ag^+]TU^3}$</td>
</tr>
<tr>
<td>$Ag^+ \ + \ 4TU \ \rightarrow [AgTU_4]^+$</td>
<td>$10^{13.57} = \frac{[AgTU_4]}{[Ag^+]TU^4}$</td>
</tr>
</tbody>
</table>

A complexation model of the concentrations of the Ag and W ionic complex species present in the electrolyte with varying pH is shown in Figure 57 for a 30 mM tungsten ion case.
Figure 57. Complex species distribution for 5 mM Ag and 30 mM W with 250 mM TU and 285 mM Cit complexing agents in the electrolyte.

Figure 58-60 shows SEM images of the surface morphology of the samples along with their respective EDS composition deposited with 30 mM, (Figure 58(a), (b)), 75 mM, (Figure 59(a), (b)), and 150 mM, (Figure 60(a), (b)), tungstate concentration at 5 mA cm\(^{-2}\) and 320 mA cm\(^{-2}\) at two different magnifications. At lower tungstate concentrations, 30 mM (Figure 58) and 75 mM (Figure 59), the morphologies are rough at the low and high current densities. A notable observation, best seen at low magnification, is that at the low current density the deposit is more compact and less porous than the higher current density case. The morphology at high magnification shows that at low current density the morphology is plate-like, while at high current density it is more dendritic and branching in nature. When larger amounts of tungstate are present in
the electrolyte there is a dramatically smoother deposit at the low current density, with a more nodular morphology (Figure 60(a)). At higher current density the morphology is again dendritic (Figure 60(b)). EDS, collected at the larger area, at low magnification, shown at the right of the SEM figures indicates the presence of oxygen and sulfur. Tungsten is expected to readily oxidize in air, thus the oxygen is due to the formation of WO$_3$ at the electrode surface. The sulfur content, from the use of the thiourea complex, was significantly lower at 5 mA cm$^{-2}$ compared to 320 mA cm$^{-2}$, for each tungstate concentration. This observation is consistent with that reported for elemental silver [13]. For example, in Figure 60 (a) at low current density the sulfur deposit concentration was 1.7 wt % (5.3 at %), while at high current density the amount of sulfur increased to 4.7 wt % (13.3 at %). It is at this current density that the highest amount of W, 18 wt %, was codeposited, relative to silver. Once exposed to air, taking into account the oxygen and sulfur content, the surface percentage of tungsten is 9.9 wt % from EDS. The EDS, a measure of the surface concentration, in contrast to the average bulk concentration from XRF, having a measurement spot size an order of magnitude larger than EDS, does confirm an increase in the W deposit wt % with the addition of tungsten ions in the electrolyte. There was no W detected by EDS in the deposit fabricated at 5 mA cm$^{-2}$ for the low 30 mM tungsten ions in the electrolyte, but W was detected for this case by XRF, 2 wt %, which suggests that the deposit composition may be non-uniform.
Figure 58. SEM images of Ag-W deposits fabricated at two different current densities with (a) 5 mA cm\(^{-2}\), and (b) 320 mA cm\(^{-2}\), in an electrolyte with 30 mM tungstate concentration; corresponding EDS spectra, collected for large area, right.

Figure 59. SEM images of Ag-W deposits fabricated at two different current densities with (a) 5 mA cm\(^{-2}\), and (b) 320 mA cm\(^{-2}\), in an electrolyte with 75 mM tungstate concentration; corresponding EDS spectra, collected for large area, right.
Figure 60. SEM images of Ag-W deposits fabricated at two different current densities with (a) 5 mA cm$^{-2}$, and (b) 320 mA cm$^{-2}$, in an electrolyte with 150 mM tungstate concentration; corresponding EDS spectra, collected for large area, right.

The mechanism of tungstate reduction during codeposition is not well established, although models in the literature for W codeposition with the iron-group elements (e.g., Ni, Fe, Co) have been presented. The earliest model, by Holt and Vaaler [42], assumed that the codepositing solid metal catalyzed the subsequent reduction of the tungstate ions based on an observation that the deposits were laminar. Younes and Gileadi [18] noted that non-laminated, solid solution alloys of tungsten with iron-group elements can also be readily electrodeposited. Another important implication of the assumption that the solid phase of the inducing metal acts as a catalyst, is that the amount of W that can be theoretically codeposited into an alloy is restricted to an inherent upper limit.

Since hydrogen evolution is always concurrent with tungsten codeposition, Oue et al. [12] attributed the tungsten reduction to atomic hydrogen, similar to what had been
introduced for the induced codeposition of Mo [17], [94]. Since both Mo and W exhibit similar induced codeposition behavior, models that pertain to Mo may also be applicable to W. Podlaha and Landolt [21] showed that the tungsten deposit concentration was not always correlated to the side reaction rate and suggested that while hydrogen may indeed play an important role in the induced codeposition mechanism it is not the governing process. In a following study and subsequent model of Mo induced codeposition with nickel ions, Podlaha and Landolt [22] showed that if the amount of the inducing element (e.g., Ni(II) ions) is much less than the amount of molybdate ions in the electrolyte then the rate of Mo deposition is limited by the concentration of Ni(II). A further increase in molybdate ion concentration in the electrolyte, or in this case tungstate ions, would not be expected to increase its rate and hence not change the deposit composition. A similar behavior can also be predicted by assuming that the inducing metal ion forms a complex or adduct with tungstate ions, a concept introduced by Younes and Gileadi [18], and Younes-Metzler et al. [10]. Both models are consistent with a limiting incorporation of W with Ag as reported by Inberg et al. [24] but not consistent with the results presented here.

In this study, the electrolyte concentration of silver ions was purposely made to be considerably lower than the tungstate ions, but yet the tungstate rate is not limited, in contrast to the former induced codeposition models [10], [18], [22]. The side reaction does indeed increase with the addition of tungstate ions and hence there is more tungsten in the deposit, which would be consistent with Oue et al. [12], but the experimental observation of the increase in sulfur incorporation with electrolyte tungstate concentration, and current density, points to a surface alkalization effect, as noted by
Oliveira et al.[29] in their electrodeposition studies with Ag-Zn alloys in a thiourea electrolyte.

Thus, the results may in fact be consistent with the Podlaha-Landolt model [22] or a model with mixed-metal complexed species[10], [18], where the reactant species change due to changes of the electrode surface pH, with a higher rate constant occurring for orthotungstate species (WO$_4^{2-}$) compared to a protonated, tungstate-citrate species (WO$_4$H$\text{CitH}_2$) with the same amount of silver ions.

A possible mechanism is listed in Equations (1) and (2) by modifying the Podlaha-Landolt model for silver, in two steps, assuming that a mixed-metal Ag-W intermediate is responsible for induced codeposition. The reacting tungstate species listed in Equation (1) is the orthotungstate species which is expected to be present when the surface is sufficiently alkaline. The silver-thiourea complex is represented as Ag(I)L.

$$\text{WO}_4^{2-} + \text{Ag}(I)L + 2\text{H}_2\text{O} + 2e^- \overset{k}{\rightarrow} [\text{Ag}(I)\text{LWO}_2]^+ + 4\text{OH}^- \quad \text{RDS (1)}$$

$$[\text{Ag}(I)\text{LWO}_2]^+ + 2\text{H}_2\text{O} + 4e^- \leftrightarrow \text{W(s)} + \text{Ag}(I)L + 4\text{OH}^- \quad (2)$$

The first step must be the rate determining one to be sensitive to a change of the tungstate species. Thus, when there is less orthotungstate species due to complexation there will be less reactant and hence a lower amount of W in the deposit. Equations (1) and (2) represent only the orthotungstate species as a reactant, and Figure 57 indicates that the surface pH would have to be at least a value 5 to generate it. Similarly, Equation (1), could be replaced by another tungstate species, but would have a different rate constant, $k$, and follow the same argument. To predict the lower amount of W in the deposit observed in Figure 54, when there is less tungstate in the electrolyte and hence less
hydrogen evolution, which would result in a lower surface pH rise, different reacting tungstate species replace the orthotungstate species in Equation (1) and the rate constant would have to have a lower value.

The Tafel slopes of the W partial current densities in Figure 55 (b) are all unusually large (over 300 mV/decade), and would not be expected for a typical metal reduction reaction. Such a large value may be a consequence of a reaction being inhibited and is consistent with the mechanism proposed in Equations (1-2). The hydrogen evolution side reaction is expected to produce adsorbed intermediates at the electrode surface. At high surface coverage, the rate of the first step would be affected and decreased by adsorbed hydrogen, thus leading to an uncharacteristically large Tafel slope.

The work presented above was published in the Journal of Electroanalytical Chemistry and is cited below:

4.4 Electrodeposition of Ag-Ni-W Alloys

In this part of the research the effect of various concentrations of the inducing metal ion, Ni and the influence of the complexing agent, citrate on the deposition behavior of Ag-W alloys is examined. The presence of different Ni-cit complex species and its influence on Ag and W deposition is presented here.

4.4.1 Effect of Ni(II) Concentration on Ag-W Electrodeposition

Figure 61

shows the polarization curves for different Ni (II) concentrations for the electrolyte presented in Table 5 at a constant RCE rotation rate of 350 rpm at pH. The total current density decreases significantly with an addition of 200 mM nickel ion concentration to the Ag-W electrolyte, and upon further addition to 400 mM the polarization curve is hardly affected. The largest change in total current density occurs at higher current...
density, greater than -0.05 A cm$^2$. The total current density at the low range (inset in Figure 61), in the potential range of (-0.3 V to -0.6 V), decreases with increasing concentrations of Ni in the electrolyte. The partial current densities from steady state analysis of the deposit composition and deposit thickness are used to help to deconvolute the different reactions reflected in these polarization curves.

Figure 61. Polarization curves of Ag-W electrolyte with varying amounts of Ni(II) in the electrolyte.

Figure 62 (a, b and c) shows the deposit composition of Ag, W and Ni in the Ag-Ni-W alloys, characterized by XRF at different applied current densities and nickel sulfate electrolyte concentrations. The composition is based on only the metallic elements. An interesting behavior is observed, with increasing Ni concentrations, the overall W content obtained in the alloy is much lower in the presence of Ni ions.
compared to the case without Ni ions for current densities below 20 mA/cm$^2$. This is unusual since Ni is known to be an inducing element for W, hence it was initially anticipated that increasing Ni concentration should result in higher W which is not seen in this case. The amount of Ag in the alloy decreases with increasing amounts of Ni ion concentration, as expected since increasing Ni concentration should result in higher Ni in the alloy. Another interesting feature in the inset of Figure 62 (b), is that an increase in W wt % is observed in the low current density region (5-20 mA/cm$^2$) with increasing concentrations of Ni to a limiting value of 4.4 wt % W at 20 mA/cm$^2$ for 400 mM Ni and then further increase in current density decreases the W wt%.
Figure 62. Composition of deposit alloy with varying amounts of Ni electrolyte concentration for (a) Ag, (b) W and (c) Ni.
The partial current densities on a log scale as a function of potential are shown in Figure 63 for (a) Ag and (b) W (c) Ni and (d) side reaction respectively. The Ag partial current density remains somewhat constant with increasing Ni ion concentration in the electrolyte and working electrode potential; this is expected since Ag is under diffusion limited control. Additionally, in the presence of Ni ions, a decrease in the Ag partial current density at more noble potentials is observed which may indicate small kinetic contribution of the Ag partial current density. With the ions to the electrolyte there is a considerable decrease in the tungsten density, which resulted in the reduced amount of W wt% in the alloy. This unexpected and interesting behavior, since the addition of Ni is expected deposition of W and not limit it. There is a substantial increase in the Ni density (Figure 63 (c)), with increase in Ni concentration in the electrolyte, which is expected and resulted in higher Ni wt % in the alloy. The addition of Ni ions also resulted in a reduction in the side reaction partial current density, which is the observed reduction in the total current density in Figure 61. Polarization curves of Ag-W electrolyte with varying amounts of Ni(II) in

the electrolyte. The presence of the dominant complexed Ni species (NiHCit and NiTU), in the Ag-W electrolyte, shifts the side reaction current density to more negative values. This behavior could be attributed to the increase in Ni species being adsorbed onto the surface of the electrode that would otherwise be occupied by adsorbed hydrogen leading to increased side reaction.
Figure 63. Partial current densities for varying amounts of Ni ion concentrations in the electrolyte for (a) Ag, (b) W, (c) Ni and (d) side reaction.
Table 15 lists the chemical equilibria equations used to generate a complexation model with varying Ni ion electrolyte concentration, with TU and citrate ligands and is shown in Figure 64 for pH 2 to point out the changes in the electrolyte species which contribute to different effects observed in composition and partial current density.

**Table 15. Reactions and Eqs used to calculate complex model**

| Reaction | Equation | Log K
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>$\text{Ni}^{2+} + \text{Cit}^{3-} \rightarrow \text{NiCit}^{-}$</td>
<td>$10^{13.5} = \frac{[\text{NiHCit}_2]^{3-}}{[\text{Ni}]^{2+}[\text{H}^+][\text{Cit}]^{6-}}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} + \text{H}^+ + \text{Cit}^{3-} \rightarrow \text{NiHCit}$</td>
<td>$10^{9.13} = \frac{[\text{NiHCit}]}{[\text{Ni}]^{2+}[\text{H}^+][\text{Cit}]^{3-}}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} + \text{H}^+ + 2\text{Cit}^{3-} \rightarrow \text{NiHCit}_2^{3-}$</td>
<td>$10^{8.11} = \frac{[\text{NiCit}_2]^{4-}}{[\text{Ni}]^{2+}[\text{Cit}]^{6-}}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} + 2\text{Cit}^{3-} \rightarrow \text{NiCit}_2^{-4}$</td>
<td>$10^{5.35} = \frac{[\text{NiCit}^{-}]}{[\text{Ni}]^{2+}[\text{Cit}]^{3-}}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} + \text{TU} \rightarrow \text{NiTU}$</td>
<td>$10^{1.42} = \frac{[\text{NiTU}]^{2+}}{[\text{Ni}]^{2+}[\text{TU}]}$</td>
<td></td>
</tr>
</tbody>
</table>

The tungsten species has only one complexed species present in substantial concentrations, at pH 2, $\text{WO}_4\text{HCitH}_3$, species and the dominant Ag ion species is complexed as $\text{AgTU}_4 (3.1 \text{ mM})$ and $\text{AgTU}_3 (1.9 \text{ mM})$ which remains unaffected with the addition of nickel into the Ag-W electrolyte. At 200 mM the nickel ions get complexed primarily with citrate ions and thiourea as NiHCit and NiTU respectively. With a further increase in Ni concentration in the electrolyte, no change in NiCit complex is observed, however, there is an increase in free $\text{Ni}^{2+}$ ions and NiTU complex. Also, the reduction in side reaction current density with the addition of 200 mM Ni coincides with the
formation of NiHCit species, as we observe no further reduction in side reaction current density with an increase to 400 mM Ni, and hence an increase in Ni-TU species.

Figure 64. Complexation model of Ni species with varying amounts of Ni concentration in the electrolyte.
4.4.2 Effect of Citrate Ion Concentration on Ni Complexation and on Ag-Ni-W Electrodeposition

In section 4.4.1, the effect of Ni concentration on the deposition of Ag-Ni-W on deposit composition and their corresponding partial current densities were examined. The change in alloy composition was related to the different complex species, coinciding with different nickel species forming with both citrate and thiourea complexes. In this section, the concentration of citrate ions in the electrolyte was varied (0.285-0.750) to complex any excess free Ni\(^{2+}\) ions and compete with the formation of the NiTU complex. In this way we could examine the role of different Ni-Cit complex species on the reduction of W species. In order to accomplish this, for a fixed concentration of Ni at 400 mM added to an Ag-W electrolyte listed in Table 5, different concentrations of citrate ions were used along with the equilibrium equations (Table 15) to build a complexation model. In this way a range of different Ni-cit complex species which would be the only dominant Ni-Cit species in the electrolyte were obtained. Figure 65 shows different Ni-Cit species dominant with different concentrations of citrate ions in the electrolyte. For a citrate concentration of 0.285 M, \(C_{\text{Ni}}^{2+}\), \(C_{\text{NiHCit}}^-\) and \(C_{\text{NITU}}^{2+}\) are all present in substantial concentrations in the electrolyte. A further increase in citrate ion concentration to 0.5 M further complexed the free \(C_{\text{Ni}}^{2+}\) and reduced the \(C_{\text{NITU}}^{2+}\). Hence the NiHCit\(^-\) species is the only dominant Ni-Cit complex species in the electrolyte. A further increase in the citrate ion concentration resulted in a NiHCit\(_2\) complex species with no NiTU present in the electrolyte. It is important to point out that increasing citrate concentration does not affect the WO\(_4\)HCit\(_3\) species.
Figure 65. Ni species distribution in the electrolyte for a pH 2 electrolyte.

Figure 66 shows the effect of citrate ion concentration in the electrolyte on deposit composition for (a) Ag, (b) W and (c) Ni. Increasing concentrations of citrate in the electrolyte resulted in a decrease in Ni wt % and increase in Ag wt% obtained with an increase in current density. No change in W wt% was observed with increasing citrate concentrations.
Figure 66. Deposit composition with varying amounts of citrate ion concentration and increasing current density for (a) Ag, (b) W and (c) Ni.

Figure 67 shows the partial current densities of (a) Ag, (b) W and (c) Ni as a function of potential, for varying amounts of citrate ions in the electrolyte. No change in Ag and W partial current density is observed, with increasing amounts of citrate ion concentration. The Ni partial current density does not change significantly at low current density and more positive potentials, but at potentials more negative than -1.0 V there is a significant decrease with increasing citrate concentration, resulting in a lower amount of nickel in the deposit. The decrease in the Ni partial current densities may be attributed to the different Ni$^{2+}$, NiHCit and NiHCit$_2$ species, each having different reaction rate constants and/or different adsorption intermediate concentrations. Since there is no change in the W or Ag rate, then the intermediate adsorbed species may be constant,
indicating that it is a change in the Ni rate constant. The subsequent decrease in the Ni partial current density decreases the Ni wt % and correspondingly increases the Ag wt% in the alloy. The effect of citrate ions and relatively the Ni-Cit complex species on the W partial current could also indicate that, since, all the Ni species in all three electrolytes examined were either complexed with citrate or thiourea at pH 2, and it has been shown that W is induced in the presence of complexed Ni species (Section 4.1-4.2), a different reduction mechanism could exist in the electrolyte containing Ag, which leads to the inhibition of W deposition.
Figure 67. Partial current densities with varying amounts of citrate ion concentration and increasing current density for (a) Ag, (b) W and (c) Ni.
According to Matlosz [95] a general model for nickel ion reduction occurs via a two-step reduction mechanism, which involves an adsorbed metal intermediate species.

\[
Ni \text{ L(II)} + e^- \rightarrow Ni \text{ L (I)}_{\text{ads}} + e^- \quad (1)
\]

\[
Ni \text{ L (I)}_{\text{ads}} + e^- \rightarrow Ni \quad (2)
\]

Recently, Sun et al. [9] showed that the Ni adsorbed species (complex or uncomplexed) played a critical role towards the induced codeposition of Mo and W.

\[
WO_4^{2-} + NiL \text{ (I)}_{\text{ads}} + 2H_2O + 2e^- \rightarrow [Ni \text{ (I) L WO}_2]_{\text{ads}}^{2-} + 4OH^- \quad (3)
\]

\[
[Ni \text{ (I)L WO}_2]_{\text{ads}}^{2-} + 2H_2O + 4e^- \rightarrow W(s) + NiL \text{ (I)}_{\text{ads}} + 4OH^- \quad (4)
\]

simultaneously with reactions (1) and (2)

For the Ag-Ni-W system, with an extension from the Ag-W system, the addition of Ni decreases the partial current density of W (Figure 63(b)), an unexpected result since nickel is known to induce the reduction of tungstate ions. Assuming reaction steps of (3) and (4) for tungsten deposition with (3) being the rate determining step, an increase in the amount of a reacting adsorbed NiL complex should facilitate the tungstate ion reduction, but no significant increase was observed in the W deposition rate or deposit composition.

With increasing concentration of citrate ions in the electrolyte, other NiL complexes are formed, (Figure 63), which suggests that the nature of the species is not significant in inducing the tungstate reduction. The change of NiL complexes can also explain why there was a subsequent reduction in the Ni partial current density, observed with increasing citrate ion concentration, making it difficult to reduce the complexes into metallic state [18], [96]. It is also necessary to point out that, even if these complexes did form, a relatively high potential would be required to reduce them further, which is usually the case when depositing Ni-W alloys from citrate electrolytes. However, in our
case, further increase in applied potential would make the deposits rougher and powdery, due to Ag reduction being under mass-transport control and hence we are limited in terms of applied potential for the Ag-Ni-W system. The reactions (1) and (2) for Ni via the adsorbed mechanism would also account for the active sites being occupied by the NiL$_{ads}$ species, which would otherwise be occupied by the [AgL (I) WO$_2$]$_{ads}^{2-}$ species, leading to W ion reduction. Thus, in this case Ni co-reduction contributes to a loss of available surface sites for W ion reduction.

In the induced codeposition mechanism suggested in the case of Ag-W alloys, the W deposition is attributed to different tungstate species being generated at the interface due to an increase in surface pH resulting from the side reaction with increasing concentrations of OH$^-$ and hence more of the orthotungstate species, WO$_4^{2-}$, in the electrolyte. This mechanism is outlined in Equations (1) and (2) from Section 4.3.1 and repeated here for convenience

$$\text{WO}_4^{2-} + \text{Ag(I)L} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow [\text{Ag(I)LWO}_2]_{ads}^{2-} + 4\text{OH}^- \quad \text{RDS} \quad (5)$$

$$[\text{Ag(I)LWO}_2]^{2-} + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow \text{W(s)} + \text{Ag(I)L} + 4\text{OH}^- \quad (6)$$

With the addition of Ni ions to the electrolyte, in the case of constant citrate ions and increasing Ni ions, the induced codeposition of W by Ni as represented in Equations (3) and (4) does not govern the behavior, perhaps due to the fact that the W ion species is already induced by silver. Ni contributes to the inhibition of W, regardless of the type of reacting species.

In summary, the Ag ion deposition governs the W deposition rate, in the presence of Ni ions; and without Ag ions, the W deposition rate is indeed induced by Ni. So, why
does the W deposition rate not depend on the codepositing Ni when Ag ions are present? One reason may be that the W ion reduction rate is thermodynamically controlled, rather than kinetically controlled and dependent upon the change of the free energy of the alloy being dominated by silver. Thermodynamic differences between Ni and Ag are evident in their very different standard potentials, $E_i^0$, with elemental Ag reduction much larger than Ni reduction. Complexation can change the ion activity, $a_i^{\text{ion}}$, changing the reversible potential, $E_{i,\text{rev}}$, the potential that occurs in the absence of current flow, representing the starting point just prior to electrodeposition. A free energy change due to alloying can occur [97], [98], thus all the metal ion reduction reactions, including W, would be influenced by the change in the solid state activity, $a_i^{\text{alloy}}$, expected to be a value less than 1 for an alloy and moving reduction potentials to more positive values. The reversible potential is given by the Nernst equation

$$E_{i,\text{rev}} = E_i^0 + \frac{RT}{nF} \ln \frac{a_i^{\text{ion}}}{a_i^{\text{alloy}}} \quad (7)$$

where the solid state alloy activity is based on the free energy of mixing according to:

$$a_i^{\text{alloy}} = e^{-\frac{\Delta G_i^M}{RT}} \quad (8)$$

While there is data available for different alloy systems at high temperature there is a lack of data for low temperature processes. Since the W partial current density in the presence of both Ag and Ni is relatively insensitive to the applied potential this would also suggest that the W rate may be thermodynamically controlled as opposed to a kinetic or mass transport control.
5.0 CONCLUSIONS

A factorial design approach towards effectively planning experiments when a large number of variables affect the deposit composition and thickness was applied towards Ni-W electrodeposition. The effect of pH, boric acid, sodium gluconate and temperature on the deposit composition (W wt %) was investigated. The composition was affected most significantly by the pH, followed by boric acid and temperature. The thickness of the deposit was found to be influenced primarily by the temperature. However, temperature had a positive influence on the W wt %, the interaction of temperature with boric acid and pH, resulted in a decrease in the wt % of W. This is a very important result to consider when designing experiments, since the individual positive effects need not necessarily result in an additive effect towards an outcome.

The effect of 2 butyne-1, 4 diol (BD) on the deposition behavior of Ni and Ni-W electrolytes in a pH 2 electrolyte was examined. Increasing concentrations of BD resulted in a decrease in Ni partial current density in the absence of W(VI) in the electrolyte, and lowering the side reaction partial current density. The reduction in deposit thickness was due to the decrease in Ni partial current density. Addition of W (VI) ions to the electrolyte exhibited an opposite behavior with increasing concentrations of BD. An increase in the Ni partial current density was observed with no substantial change of the W partial current density. This resulted in Ni rich deposits with increasing concentrations of BD. Thinner deposits resulted with an increase in BD concentration. In order to improve current efficiency, a higher pH electrolyte was examined. The Ni-W electrolyte at pH 8 exhibited the same behavior polarization behavior as the pH 2 electrolyte. From the partial current density analysis, it was found that both the Ni and W partial current
densities reduce with increasing BD concentrations at pH 8. However, a larger order reduction in W partial current density resulted in Ni rich deposits. The deposit thickness improved marginally compared to Ni-W deposits at pH 2. The deposits obtained from a pH 8 electrolyte were brighter compared to pH 2 Ni-W deposits. The effect of boric acid to improve deposit thickness and efficiency was examined from a Ni-W electrolyte at pH 8 with 5 mM BD. Increasing boric acid concentration to 500 mM resulted in a shift in the side reaction partial current density to more cathodic potentials and an increase in Ni and W partial current density. Further addition of boric acid to 1 M did not affect the deposit composition and thickness. The addition of boric acid also improved the uniformity of the Ni-W deposits by eliminating the streak patterns observed in non-boric acid Ni-W electrolytes at pH 2 and pH 8, that are created by the air agitation of the electrolyte. A higher electrolyte temperature was examined to improve the current efficiency, including boric acid and 5 mM BD in the Ni-W electrolyte at pH 8. Increasing the electrolyte temperature to 60 °C improve the deposit thickness drastically, even though the side reaction partial current density increased. This improved efficiency was attributed to the increased metal deposition rates.

The effect of sulfur incorporation into the Ni-W deposit was investigated with varying amounts of thiourea as a sulfur source. Small additions of thiourea < 65 mM resulted in brighter deposits, while a further increase in concentration resulted in dark metallic and powdery deposits at higher applied current densities. The S wt % increased significantly with increasing thiourea concentrations, with a relative decrease in Ni wt %. The W wt % was below 10 wt % and remained unaffected with increasing thiourea concentrations. A complexation model was used to examine the distribution of the Ni
complex with increasing amounts of thiourea. The increase in thiourea resulted in the complexation of free Ni\textsuperscript{2+} ions in the electrolyte, and hence is attributed to the increase in S content in the deposit.

Silver-tungsten compounds with sulfur were electrodeposited from a thiourea-citrate electrolyte having a high W wt % than previously reported. The reduction of tungsten, an example of induced codeposition, relies on other elemental ions to help it to reduce, suggesting that if the inducing elemental ions are in low concentration it would limit the W partial current density. The data presented here suggests that this is not the case. With a low concentration of Ag ions in the electrolyte the tungsten ion deposition increased with added sodium tungstate. Also, the side reaction increased with added sodium tungstate between, 0-75 mM, but then no further increase was observed with 150 mM of tungsten ions. At pH 2 the tungsten ions in the electrolyte are expected to be complexed with citrate in a protonated form, but higher amounts of W in the deposit are expected to be deposited with a higher surface pH with a change in the type of tungsten ions being reduced. The larger quantities of tungsten in the deposit were accompanied with higher amounts of sulfur. Scanning electron microscopy analysis showed a change in surface morphology of the deposits with added tungsten ions with smooth deposits appearing only at the higher tungsten ion electrolyte concentration (150 mM) and at low current density. Dendritic deposits were found at high current density irrespective of the amount of tungsten ion concentration.

A ternary alloy Ag-Ni-W system from a single stable electrolyte has been presented for the first time. Galvanostatic deposition was used to investigate the effect of current density on deposit composition and the relative metal partial current densities. In
general, Ag-rich deposits were obtained at low current densities < 20 mA/cm², while an increase in current density led to an increase in the Ni wt %. The addition of Ni concentration in the electrolyte on the deposition behavior of Ag-W alloys and W wt% in the alloy was investigated. Interestingly, the addition of Ni ion concentration did not increase the W partial current density as expected since Ni is an inducing element, but rather decreased the W partial current density. An increase in Ni wt % in the alloy was attributed to an increase in the Ni partial current density which was expected with an increase in Ni ion concentration in the electrolyte. The effect of citrate ion concentration was investigated, to examine the effects on deposit composition, and as a way to probe the importance of the Ni ion species. Using the complexation model, the effect of three different dominant Ni-Cit complex species on W was investigated as a result of increasing citrate ion concentration in the electrolyte. Increasing citrate concentration from 0.285 M to 0.5 M, shifted the dominant species from Ni²⁺ and NiHCit⁻ ions to only NiHCit⁻ dominant in the electrolyte. Further increase in citrate concentration to 0.750 M resulted in only the NiHCit₃⁻ species being dominant in the electrolyte. No change in the partial current densities of W and W wt % was observed. An interesting result here was that none of the complexed Ni-citrate species were able to further induce W deposition. In the presence of Ag ions, the W deposition rate was not influenced when Ni ions were introduced into the electrolyte, which is an interesting result, since Ni acts as an inducing metal for W deposition. The deposition potential also did not affect the W deposition rate, which points to the fact that a different phenomenon due to a thermodynamic shift in the reduction potential of W might be responsible for W deposition in the ternary electrolyte.
6.0. RECOMMENDATIONS

I. The influence of BD during Ni-W deposition indicated that BD affected the Ni partial current density in both low and high pH electrolytes. Results obtained could be due to, the adsorption of BD onto the metal surface or due to the mass transport limitation due to the low concentration of BD in the electrolyte. One could then vary the agitation rate during deposition to investigate if the effects are solely due to the mass transport effects with respect to BD concentration. A rotating cylinder electrode is recommended to investigate this behavior, as the RCE has much better control over the hydrodynamic environment.

II. Although, pH 2 electrolyte was determined to be stable for the electrodeposition of Ag alloys, low pH electrolytes lead to low current efficiencies due to the high concentration of H\(^+\) ions in the electrolyte, due to the reaction below

\[2H^+ + 2e^- \rightarrow H_2\]

The concentration of H\(^+\) ions at pH 2, given by \(H = 10^{-\text{pH}}\) is 0.01 M, which is 20 times higher than the Ag\(^+\) ions in the electrolyte. This causes the limiting current of Ag to be much than the H\(^+\) ion limiting current, leading to higher side reactions resulting in lower current efficiencies and rougher deposits at higher applied current densities. One way to tackle this, is to either increase the Ag ion concentration in the electrolyte, much higher than 0.01 M at pH2 or to increase the electrolyte pH. However, increasing the pH too high might lead to electrolyte instabilities, one would recommend using the complexation model as a guide to determine an optimum pH required to improve current efficiency, and obtained a wide range of metallic compositions in the deposit.
III. The effect of W concentration on Ag-W deposit composition was examined. One could examine if increase in Ag ions in the electrolyte affect the W wt % in the deposit. Since the concentration of Ag is under limiting control 0.005 M, while tungsten at high concentration is expected to be under kinetic control, it would be interesting to examine if the W deposition is limited by the Ag ion mass transport. An increase in rotation rate would lead to an increase in the limiting current of Ag, one should first examine if a drastic increase in rotation rate has a large significant effect on the limiting current. If not, then another way to increase the limiting current for Ag would be to increase the concentration of Ag ions in the electrolyte, along with increase in rotation rate. Now, if an increase in deposition rate of W is observed, along with an increase in Ag deposition rate, then a coupled effect between Ag and W exists and this could be used to tailor deposit composition.
7.0 REFERENCES


