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**Diverse electrodeposits from modified acid sulphate (Watts nickel) baths**

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**Abstract**

A diverse range of nickel-based coatings can be cathodically deposited from a classical Watts electroplating bath containing suitable additives by appropriate control over operational conditions. Modern nickel-based electrodeposits are concisely reviewed and can be seen to be longer-term developments from the publication of optimised conditions for rapid nickel plating from an acid sulphate bath by Watts in 1916. Recent examples of tribological nickel electrodeposits are illustrated by examples from the authors’ laboratory: i) low friction, hard, wear resistant surfaces (containing 2-D, layered, self-lubricating particles of Ni-P-MoS2), ii) superhydrophobic layers of Ni-WS2, showing a lotus petal effect (for self-cleaning surfaces), iii) light emitting, luminescent signal bearing surfaces of Ni-BAM (BaMgAl11O17:Eu2+) metal oxide, (providing an in-situ phosphor wear tracer) and iv) nanocrystalline surfaces of Ni, Co, Ni-Co and Ni-Co-P (including high surface area electrocatalysts). Important trends in the deployment of the longstanding, versatile Watts nickel electroplating bath are seen to include the development of a) surfaces having tailored structure hence special properties by choice of bath composition and operational conditions, b) nanostructured composite layers containing mixed inclusions and c) layers able to diagnose in-service wear and provide an output signal. Subject areas needing further research are suggested.

**Keywords:** additives;lubrication; nanostructure, surface tension; tribology.

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(Approx. <6,400 words, 36 references, 0 tables, 7 figures).

**1.** **Introduction**

A wide range of coatings can be cathodically deposited from an undivided Watts nickel based electroplating bath containing suitable electrolyte by appropriate control over operational conditions, including the temperature, current density and degree of agitation. A typical Watts nickel plating bath might contain 300 g dm-3 NiSO4.7H2O, 45 g dm-3 NiCl2.6H2O and 45 g dm-3 boric acid, with a pH 4.5 operating at a temperature of 60 oC. Since pioneering work in the early 1900s (Figure 1) and the publication of an optimised electrolyte and process conditions by Watts [1], such baths [1-3] have benefitted from extensive laboratory and industrial work over the last century [4, 5], including classical studies of levellers and brighteners [6]. The inclusion of suspended nanoparticles in the deposits results in high performance coatings for tribological engineering applications.

Composite coatings containing metallic, ceramic or polymeric included particles have developed over 30 years [7-9], including the use of nanoparticles [9]. Such deposits combine colloid chemistry and electrophoresis, sometimes with abrasion and ultrasound [10] to assist deposition, providing an expanding suite of advanced coatings [11,12], including multifunctional ones. Nickel electrodeposits have played a strong role in the history of electroplating and engineering coatings, particularly in tribology [13]. This is understandable, since stable baths, particularly Watts nickel ones based on nickel sulfate and nickel chloride with a boric acid pH buffer, are classical, additives and operational conditions are well established and electroplating offers a controlled, versatile production technique having moderate costs and requiring simple facilities. At present, the dominance of nickel coatings is under increasing pressure from environmental concerns or health and safety restrictions [14]. Nevertheless, modern nickel-based electrodeposits remain readily scaled, industrially competitive and of scientific importance, partly due to progress in the development of controlled microstructure, and nanostructure.

Important control parameters (Figure 2) include bath composition, particularly additive type and level, operating conditions (such as temperature, current density and electrode/electrolyte movement), electrode stimulation (e.g., rotation, reciprocation, wiping, or abrasion) electrolyte agitation (including jet flow and ultrasound), the presence of suspended/electrically charged particles (metal, polymer or ceramic) in the bath and the type of electrical control at the cathode (potentiostatic, constant current, smooth direct current or pulsed direct current). Examples of families of modern, nickel-based electrodeposited coatings (Figure 3) include i) compositionally modulated, e.g., gradient layers, ii) multilayers having different compositions and iii) composite coatings containing at least one other phase (metal, ceramic or polymer) in addition to the electrodeposited metal matrix.

**2. Examples of developments in nickel electrodeposits**

**2.1 Composite deposits**

Nickel-graphite composite coatings have been studied for their controlled tribological and electrical properties. For example, a Watts nickel bath containing 297 g dm-3 NiSO4.6H2O, 50 g dm-3 NiCl2. 6H2O and 35 g dm-3 H3BO3 at pH 3.5 was used in a stirred beaker cell at a temperature of 333 K with vertical electrodes and a cathode current density of 10 mA cm-2 by Brenska-Justkowiak *et al.* to produce 1-20 m thick Ni-C layers of controlled electrical resistance on mild steel substrates [15]. The morphology of the deposits was examined by scanning electron microscopy and electrochemical impedance spectroscopy, EIS was used to study through porosity in the coatings in 1 mol dm-3 H2SO4 at 296 K. The coating porosity was estimated to be 0.02, 0.16 and 81% in 10 m, 5 m and 1 m thick coatings using a frequency scan. Under the experimental conditions, the authors considered that an area resistance below 500 ohm cm2 indicated pin holing and pointed the way to a simple and rapid, 2-point, fixed frequency EIS porosity test.

Lapinski *et al.* utilised controlled electrolyte flow in a vertical rectangular channel to study dilute Ni-C layers on mild steel [16]. Unusually, the authors used 3 cells:

a) a beaker cell with a magnetic bar stirrer rotated at up to 500 rpm. The steel or Ni coated steel plate, typical size 6 cm×5 cm being placed parallel to and equidistant from two 10 cm × 6.5 cm Ni anode plates placed on either side of the cathode,

b) a commercial Hull cell stirred by a magnetic follower at 300–500 rpm. The cathode plate was 11 cm×7 cm and the Ni anode was 6 cm×6 cm while the insulating walls were 12 cm and 5 cm, and

c) a purpose-built, parallel plate flow cell containing 4 cm × 5 cm nickel anode and steel cathode plates, flush-mounted in the walls of the acrylic flow channel and the interelectrode gap was 1 cm. The flow channel had entry and exit lengths to smooth the flow regime and achieve mean linear flow rates of 10–25 cm s−1.

The authors sought to achieve a surface with separated, single particles of graphite which were uniformly dispersed. While appropriate electrolyte conditions were considered important, the study highlighted the particle content in the bath and the need for efficient and uniform mass transport over the whole surface to be coated as the key parameters for determining the loading and distribution of graphite particles. By controlling these parameters, the distribution of graphite particles over the entire coated surface was uniform provided that the flow and mass transport regimes were controlled in a flow cell. It is interesting to note that an anionic (naphthalene sulfonate surfactant was used in a graphite dispersion in these studies (at a level of 10 mg surfactant g-1 graphite, resulting in a deliberately low content of relatively large (2 m) graphite inclusions. This may be contrasted with the majority of electrodeposited nickel composites. Where a cationic surfactant is used in the bath to achieve relatively high included particle levels in the deposit [7-10].

Several trends may be illustrated by Ni-SiC composite coatings. Several workers have considered increasingly smaller particle sizes, such inclusions being easier to suspend in the electrodeposition bath and providing harder, more compact and perhaps more uniform composite deposits. The importance of particle size was considered by Garcia *et al.* [17]. SiC particles of 5, 0.7 and 0.3 m, were codeposited with nickel from a Watts nickel bath. For a given number density of particles in the plating solution, the number density of particles in the coating increased at smaller particle size. The friction and wear behaviour of these composite coatings was evaluated in uni- and bi-directional sliding tests against corundum balls. The best sliding wear resistance was obtained with Ni–SiC composite coatings containing 4–5% vol. submicron SiC particles.

Few workers have adequately considered the importance of the electrical charge on the colloidal particles dispersed in the bath. The point of zero charge (PZC) of SiC nanoparticles was determined by means of a standard potentiometric titration method, while the influence of the main technological parameters on the microstructure of an electrodeposited Ni-SiC composite film were studied and optimized. The results showed that a high bath pH favoured negatively charged SiC nanoparticles while a high bath temperature rendered them positively charged. Under the experimental conditions, sodium dodecyl-glycol was shown to be an effective anionic surfactant. The particles had a nett positive charge, encouraging electrophoretic migration to the cathode. The optimized Ni-SiC composite contained 100 nm particles, which were uniformly dispersed [18].

Composite coatings suitable for protection against corrosion were prepared by electrodeposition of a chloride-nickel coating containing silicon carbide particles maintained in the suspension [19]. The authors used a bath containing 0.1 mol dm-3 NiCl2.6H2O, 0.4 mol dm-3 NH4Cl, 0.1 mol dm-3 NaCl and 0.3 mol dm-3 H3BO3 at pH 3.5 and 45 oC. A current density of 2 A dm-2 was used over a deposition time of 60 minutes. 10 and 20 g dm-3 SiC loadings were favoured, with 50 g dm-3 bath levels being explored. The Ni-SiC composite coatings showed a better corrosion resistance in 0.6 mol dm-3 NaCl solution and high hardness than nickel, electrodeposited under the same conditions. The coatings were uniform and adherent to the substrate. X-ray diffraction showed the nickel coatings to have a (111) preferred orientation.

Submicron (150–500 nm) SiC inclusions in electroplated nickel deposits were considered by Walsh *et al*. [20]. This study used a modified Watts nickel electrolyte at 60 oC containing 2 g dm-3 coumarin at current densities from 1 to 10 A dm-2 under well-stirred electrolyte conditions to screen 17 surfactants, including cationic, anionic and non-ionic types, to produce uniform included particle deposits, typically <10 m thick, containing 5-54% vol. SiC. The authors found that the composite coatings showed improved resistance to abrasive wear, compared to a plain nickel deposit, by a factor of 2 to 20. The composite deposit showed similar internal (lightly compressive) stress levels to plain nickel.

Prior to the production of Ni–SiC composite coatings, the effects of particle size, particle content, the pH of the electrolyte, temperature, current density and electrolyte stirring rate on the amount of SiC deposited in the nickel layer were investigated in a sulfamate bath at a pH of 4.0 and a temperature of 50 oC [21] although the quantitative rationale for controlling the particle content in the deposit was unclear. Both stirring speed and current density affected SiC content in the deposit. A bath particle loading of 50 g dm-3 was used, with a stirring speed of 500 rpm. Ni–SiC composite layers having a SiC particle size of 14.0 m were produced. By manipulating the current density and the plating time, bilayer Ni–SiC composite coatings containing low and higher SiC content were produced. Their mechanical properties were evaluated by micro-indentation hardness tests. A Ni–SiC layer with a low, typically <5.4 vol.% of SiC, was obtained by plating for 30 minutes at a current density of 10 A dm-2. A Ni–SiC layer with a higher SiC content, <24.6 vol.% of SiC could be achieved by plating at 1 A dm-2 for 5 hours. The effect of particle size, particle level, bath pH, temperature, current density and stirring rate on the amount of SiC deposited in the Ni layer were investigated. By controlling the current density and the plating time, bilayer Ni–SiC composite coatings were produced and their mechanical properties were evaluated by micro-indentation hardness tests [21].

One of the few electrolytes to compete with Watts nickel for specialised high speed electroplating or electroforming is the nickel sulfamate bath. Nickel coatings containing included poly(methylmethacrylate) - Ni-PMMA coatings were studied by Goods *et al.* to achieve dispersion-hardened composite coatings for microsystems [22]. The electrodeposits were fabricated using lithography, electroforming, and moulding (LIGA) in a sulfamate bath containing a suspension of 10 nm diameter Al2O3 particulates. Mechanical properties were compared to baseline specimens fabricated using an identical sulfamate bath chemistry without the particulates. The authors claimed that the as-deposited oxide dispersion strengthened nickel exhibited significantly higher yield strength and 50% higher tensile strength than the baseline material. This increase in as-deposited strength was attributed to Orowan strengthening, i.e., an increase in the intrinsic resistance to dislocation movement due to dispersed inclusions in the microstructure. The composite deposit also showed improved retention of room-temperature strength after annealing over a range of temperatures up to 600 °C. Nanoindentation measurements revealed that the properties of the dispersion-strengthened deposit were uniform through its thickness, even in narrow, high aspect ratio structures. Microscopy revealed that this resistance to softening was due to an inhibition of grain growth in the presence of the oxide dispersion. At elevated temperatures, the strength of the oxide dispersion strengthened nickel, ODS-Ni was approximately 3 times greater than that of the baseline material albeit with a significant reduction in hot ductility.

Bercot *et al.* deposited Ni-PTFE composites from a sulfamate bath [23]. When stirring was carried out using a rotating disk electrode, well-defined laminar flow allowed a classical model proposed by Guglielmi, to be modified to rationalise results for Ni–PTFE deposition by incorporating a correction based on the speed of magnetic rotation.

**2.2 Pulsed current electrodeposition**

Asymmetrical pulse waveforms were studied by El-Sherik *et al.* [24]. Square-wave cathodic current modulation was used to electrodeposit ultra-fine-grained nickel from an additive-free Watts bath. The influence of the pulse parameters (pulse on-time, off-time and peak current density) on the grain size, surface morphology and crystal orientation was determined. The study showed that an increase in peak current density resulted in considerable refinement in crystal size of the deposit. The crystal orientation progressively changed from an almost random distribution at the lowest peak current density of 400 mA cm-2 to a strong (200) texture at a peak current density of 1600 mA cm-2. At constant peak current density and off-time, the crystal size of the deposit was found initially to decrease at longer pulse on-time before it started to increase with further increase in the on-time. The crystal orientation progressively changed from an almost random distribution at the shortest n-time of 1 ms to a strong (200) fibre texture at an on-time of 8 ms. An increase in the pulse off-time at constant on-time and peak current density resulted in a progressive increase in crystal size. However, the crystal orientation remained unaffected with increasing off-time.

The synthesis of nanocrystalline nickel by electrodeposition has been studied for more than 10 years. However, most attention has been on the adjustment of bath composition or development of new chemical additives. Qu *et al*. developed a procedure to achieve a nanocrystalline nickel deposit from an additive-free bath [25]. Pulse plating with ultra-narrow pulse width and high peak current density was employed to increase the deposition current density and the nucleation rate. With an on-time of 10 ms and an off-time of 90 ms, various surface morphologies, grain sizes, textures, and hardness were obtained at different current densities. Grain sizes ranging from 50 to 200 nm were obtained when the current density varied from 300 to 60 A dm-2. The preferred orientation of the nickel deposit changed from a weak (200) fibre texture to a strong (200) fibre texture when the peak current density increased from 40 to 100 A dm-2. The intensity of the (200) fibre orientation decreased when there was a further increase in the current density. The hardness of the nickel deposit was also found to increase at higher peak current density when it changed from 20 to 150 A dm-2, but the hardness tended to fall when the current density was above 150 A dm-2. These experimental findings are considered to relate to the change in cathode overpotential which affects both the grain size, the internal stress, the porosity, and the preferred orientation.

Four examples of nickel electrodeposit families (and their applications) can be considered:

a) Low friction, hard, wear resistant surface (containing 2-D, layered, self-lubricating particles of Ni-P-MoS2),

b) Superhydrophobic layers of Ni-WS2, showing a lotus petal effect (for self-cleaning surfaces),

c) Light emitting, luminescent signal bearing surfaces of Ni-BAM (BaMgAl11O17:Eu2+) metal oxide, (providing an *in-situ* phosphor wear tracer) and

d) Nanocrystalline surfaces of Ni, Co, Ni-Co and Ni-Co-P (including high surface area electrocatalysts).

These examples are concisely illustrated by examples from our laboratory in the following sections.

**3. Low friction, hard, wear resistant surfaces**

MoS2 based composite coatings have being highly required in surface engineering to achieve low-friction. A Ni-P/MoS2 composite coating has been deposited on mild steel by a combination of electrodeposition bath and electrophoresis from a hypophosphite ion containing Watts nickel bath; key operational parameters for successful electrodeposition have been studied [24[. Too high a current density caused the formation of cracks in the coating due to the high internal stress produced. Cetyltrimethylammonium bromide, CTAB and particle concentrations in the bath significantly affected the content of MoS2 content of the deposit, producing a maximum particle content of 11.8% wt. A 3D-SEM image showed a wide range of average surface roughness from 2.8 to 8.9 μm. The addition of MoS2 affected the deposition rate at different sites, resulting in a roughened surface showing clusters of nodules. Figure 4 shows the friction coefficients with time for the substrate, a Ni-P deposit and various Ni-P composite coatings. The friction coefficient of the substrate increases gradually in the first 100 s and then varies between 0.5 and 0.65 during the remaining test time. The pure Ni-P coating produced a lower friction coefficient around 0.4. For the Ni-P/MoS2 0.3 g dm-3 coating, the coefficient of friction remains relatively constant at 0.2 for hundreds of seconds then rises slowly to 0.5. The composite coating deposited at 10 g dm-3 shows the lowest and steadiest friction coefficient of 0.05. The Ni-P/MoS2 coating showed a lower friction as the particle concentration increased in the bath, the Ni-P/MoS2 10 g dm-3 achieving the lowest friction coefficient.

**4. Superhydrophobic, self-cleaning surfaces**

Superhydrophobic surfaces have been intensively investigated for applications requiring self-cleaning and corrosion resistance. The techniques used to fabricate such a coating tend to be costly, time and energy consuming; further surface modification steps are often needed. In this study, a superhydrophobic composite electrodeposit based on a tungsten disulphide nanoparticles dispersed in nickel on a mild steel substrate was successfully developed in a single-step, one-pot process by Zhao *et al.* [27]. Figure 5 shows the variation of water contact angle on the deposit surface as a function of WS2 content in the deposit. At 25 oC, the deposit showed a water contact angle of 158.3 deg and a sliding angle of 7.7 deg. The effects of operational parameters on surface morphology and superhydrophobicity are discussed. The surface of the as-prepared deposits exhibited good self-cleaning and corrosion resistance, providing the potential for industrial applications as specialised engineering coatings.

**5. Light emitting, luminescent signal bearing surfaces**

A composite luminescent Ni coating containing embedded blue-emitting rare-earth mixed metal oxide (BaMgAl11O17:Eu2+) phosphor particles has been electrodeposited for the first time in an aqueous electrolyte with a cationic surfactant, CTAB and a non-ionic surfactant, PEG (polyethylene glycol) additive by He *et al.* [28]. Operational parameters including particle concentration and additive level on the degree of phosphor doping into the deposits have been studied. Figure 6a) shows blue coloration on the coating surface recorded under UV light. Under fluorescent microscopy, Figure 6b) shows the phosphor particles to be well distributed. Fluorescent microscopy was used to detect the luminescence of the Ni-phosphor coatings using a DAPI filter (excitation, 350 nm; emission, 450 nm). Figure 6c) shows the corresponding photoluminescence spectra of composite coatings excited at 330 nm. The emission wavelength of Ni-phosphor (BMA:Eu2+) samples were always around 450 nm and the spectra shape did not shift as the amount of phosphor particles in the electrolyte increases. The luminescence intensity of the coating is mainly related with the coverage of phosphor in coating. The luminescence intensity of the coating at bath levels of 5 g dm-3 phosphor is 10 times higher than that with 2 g dm-3, compared to the doubling of particle coverage. The intensity dropped to a slightly lower level at 8 g dm-3. The luminescence emission is much weaker when the particle concentration is 10 g dm-3, although the area coverage was 9.5%. This is attributable to a high concentration of impurities in agglomerates, the energy of luminescence easily migrates to these sites and leads to lower intensities of the Ni-phosphor coating. Figure 6f) shows the hardness of the composite coatings as a function of particle concentration in the electrolyte. The hardness of the substrate was 260±20 HV, in agreement with values for mild steel. The pure Ni coating had a hardness of 450±15 HV. For Ni luminescent coatings, the hardness values increase substantially in the range of 498 to 599 HV. The addition of BMA: Eu2+ phosphor particles reinforced the Ni deposit. According to XRD data, the composite coatings had an ultrafine grain size from 7 to 10 nm compared to the grain size of 18 nm for the pure Ni coating, so the hardness increase of the composite coatings over conventional Ni coating can mainly be attributed to the Hall–Petch hardening effect, the hardness value increase with decreasing grain size. However, there is no significant change in grain size for the composite coatings deposit at different particle concentrations, so the Hall–Petch effect cannot explain the hardness variation of composite coatings. For composite coatings, the coating with higher particle content shows the higher hardness. The strengthening effect could be explained in terms of an Orowan hardening mechanism, where dislocations bow around phosphor particles which act as dislocation pinning sites resulting in an increase in the flow stress. The coating deposited at a 5 g dm-3 phosphor concentration in the electrolyte showed the highest value of 599±29 HV, consistent with the maximum amount of particles incorporation seen in the coatings. These luminescent coatings show improved hardness and corrosion performance compared to a pure Ni electrodeposit. The illumination intensity of the coating was proportional to the phosphor coverage on the coating. Such luminescent coatings work well as a stand-alone, blue indicator layer in a multi-layer coating system to give early warning of coating failure or to diagnose in-service wear conditions.

**6. Nanocrystalline surfaces**

Nanocrystalline surfaces can be achieved by control of bath composition, particularly additive type and level, together with the use of suitable operational conditions (including temperature, current density, direct current waveform and electrode/electrolyte movement, including the use of ultrasonic stimulation.

The rate ofgrain growth in nanocrystalline nickel electrodeposits was studied by transmission electron microscopy and differential scanning calorimetry at different heating rates [29]. On annealing, the nanocrystals appeared to grow abnormally and released 416 J mol-1 of heat. The mechanism of the abnormal grain growth was attributed to the coalescence of subgrains. The method for determination of the grain growth activation energy as well as all the other kinetic parameters in the Johnson-Mehl-Avrami equation was proposed, based on an isokinetic analysis, this method is applicable to general types of transformation process governed by a single activation energy under the isokinetic condition. The activation energy for the grain growth of nanocrystalline nickel electrodeposits was found to be *ca.* 131.5 kJ mol-1 using this method. The difference between the present method and the Kissinger and Ozawa method was addressed in terms of their physical backgrounds.

In the case of single metal nickel electrodeposits, a high chloride bath was examined by Recio *et al.* [30]. Following cleaning, the stainless steel substrate was electrodeposited with a very thin layer of Ni from a ‘Woods strike’ containing 100 cm3 dm−3 concentrated HCl and 240 g dm−3 NiCl2 at a current density of 100 mA cm−2 for 60 s then nickel was deposited at 60 oC from a Watts bath containing 260 g dm−3 NiSO4, 50 g dm−3 NiCl2 and 30 g dm−3 HBO3, at 100 mA cm−2 for 180 s, producing a deposit of *ca.* 5 m thickness. Mass transfer of ferricyanide ion to a high surface area, nanostructured nickel electrodeposit on a planar electrode was measured in a rectangular flow channel. The limiting current was up to 11 times higher than that experienced on a smooth nickel plate at a mean linear electrolyte flow velocity of 6 cm s-1 (Figure 6). The coatings have been used as electrocatalysts in fuel cells, batteries and electrosynthesis reactors.

Broad similarities in the electrochemistry of nickel and cobalt enable cobalt analogues of Watts nickel baths or Ni-Co alloy baths to be readily developed, including electrolytes aimed at producing nanocrystalline deposits. Three reviews have been published highlighting hardness, corrosion resistance and wear characteristics of engineering coatings from undivided cells: a) single metal Ni and Co [31] deposits, b) binary Ni-Co alloy [32] deposits and c) ternary Ni-Co-P alloy [33] deposits. Nanostructured nickel shows very high active electrode area in flow cell mass transport studies [30], while Ni-Co demonstrates impressive hardness, wear resistance and an acceptable friction coefficient against steel [34-36].

**7. Summary**

1. Despite environmental pressures and health and safety limitations, nickel electroplating continues to be important in realising important fundamental research and industrial coatings for engineering applications.

2. The stable and versatile Watts nickel bath, developed over a century ago, has remained the basis for most research and production nickel plating. Continued advances in the electrodeposition of nickel often utilise the Watts bath as a platform to realise modern engineering coatings. Few baths have competed against the versatility of Watts nickel; the sulfamate bath has sometimes been preferred for high speed plating and electroforming.

3. Electrodeposition of nickel offers considerable versatility. Control of electrolyte composition (metal ion source, indifferent electrolyte, pH buffer and additives), electrode/electrolyte geometry (static or moving cathode; electrolyte flow; ultrasound; cathode abrasion) and operational conditions (temperature, electrolyte agitation, current density and mode of current control). Such versatility offers good control of deposit composition, microstructure and nanostructure hence physicochemical and tribological properties.

4. Examples of recent nickel-based electrodeposits (and their targeted applications) include:

a) Low friction, hard, wear resistant surface containing 2-D, layered particles of Ni-P-MoS2, (lubrication),

b) Tough, superhydrophobic layers, showing the lotus petal effect of Ni-WS2 (as robust, self-cleaning surfaces).

c) Light emitting, luminescent signal bearing surfaces of Ni-BAM (BaMgAl11O17:Eu2+) metal oxide, (as in-situ phosphor wear tracer) and

d) Nanocrystalline surfaces of Ni, Co, Ni-Co and Ni-Co-P, (as high surface area electrocatalysts).

5. Important trends in electrodeposited nickel coatings are seen to be the development of a) surfaces having tailored structure hence special properties by choice of bath composition and operational conditions, b) nanostructured composite layers containing mixed inclusions and c) layers able to diagnose in-service wear and provide an output signal.

**8. The need for further research**

1. The comparative cost and performance of nickel-based deposits from traditional, developing and competitive coating techniques require strategic evaluation, particularly for complex tribological loads in aggressive environments in the light of most research being performed on simple, freshly prepared electrolytes under controlled load conditions, often in moderate environments.

2. The ageing of bath chemistry and the changing performance of deposits during in-service duty both need quantitative evaluation.

3. Newer electrolytes enabling advanced coatings while being able to meet the cost, availability, stability and handling demands of industrial processing together with ease of scale-up.

4. The mechanism and interaction of electrolyte additives are critical to realising next generation electrodeposits able to meet the increasing challenges of real tribological environments.

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**Figures**

**Figure 1.** A time-line for electrodeposition from Watts Nickel baths, highlighting important milestones.

1833/34 Faraday’s laws of electrolysis published.

1837 Bird deposited nickel on Pt from nickel chloride or sulfate solution.

1840 Shore patented a nickel nitrate bath.

1843 Bottger developed first bath based on nickel and ammonium sulfates.

1868 Remington developed an ammonium chloride based Ni bath and Ni pellet anodes in a basket.

1869 Adams developed and patented a commercial Ni bath using ammonium nickel sulfate.

**1916Watts published a paper on an optimised bath for raid nickel plating [1].**

1934 Schlotter marketed a bright ‘Watts’ Ni bath using organic additives.

1939 Cambi and Piontelli patented a nickel sulfamate bath.

1945 DuRose introduced a coumarin containing semi-bright Ni bath.

1957- Watson & Edwards levelling and brightening studies.

1970- Development of modified Watt’s Ni baths for composite plating.

1980- Introduction of superhydrophobic, self-cleaning coatings.

1980s- Development of self-lubricating, layered inclusion composite Ni (and Co) coatings.

2013 Mass transport and area measurements of nanostructured nickel deposits in a rectangular channel flow cell [30].

Further details on early studies are available in references [1-4].

**Figure 2.** Important control parameters in electrodeposition of modern nickel coatings, including bath composition, particularly additive type and level, operating conditions (such as temperature, current density and electrode/electrolyte movement), electrode stimulation (e.g., rotation, reciprocation, wiping, or abrasion) electrolyte agitation (including jet flow and ultrasound), the presence of suspended/electrically charged particles (metal, polymer or ceramic) in the bath and the type of electrical control at the cathode (potentiostatic, constant current, smooth direct current or pulsed direct current).

**Figure 3.** Examples of directions in advanced nickel electrodeposits. BAM: barium aluminium magnesium oxides (a luminescent phosphor).

**Figure 4.** Friction coefficient as a function of time for different surfaces sliding against a stainless steel ball, highlighting the performance ofa hard, wear resistant deposit containing layered, self-lubricating particles of Ni-P-MoS2 deposited for 45 minutes at 2.5 A dm-2 from a Watts nickel bath at 60 oC containing0.1 g dm-3 cetyltrimethyl ammonium bromide. The bath loading of MoS2 is indicated. After He *et al.* [28].

**Figure 5.** Water contact angle on the deposit surface as a function of WS2 content in the deposit for superhydrophobic, self-cleaning coatings of Ni-WS2. After Zhao *et al.* [27].

**Figure 6.** Photoluminescence emission spectra of Ni-phosphor coatings deposited for 30 minutes from solutions with different particle concentrations: 2 g dm-3, 5 g dm-3, 8 g dm-3, 10 g dm-3 (*t* = 45 min, *j* = 4 A dm-2). (b) Fluorescence image of Ni-BMA=Eu2+ coating deposited in the presence of PEG and CTAB electrolyte additives (*t* = 45 min, *j* = 4 A dm-2, *c* = 5 g dm-3 under 365 nm UV illumination. c) After He *et al.* [28].

**Figure 7.** Enhanced area nanocrystalline nickel deposits from a high chloride bath. The limiting current enhancement factor (compared to a smooth nickel surface) *vs*. velocity is shown for: () nanostructured nickel electrodes in the presence of a plastic mesh turbulence promoter, (o) nanostructured nickel electrodes in the absence of a promoter and () a flat, planar nickel electrode. Reduction of ferricyanide ion from 10 mmol dm-3 ferricyanide in 1 mol dm-3 Na2CO3 at 25 oC, using a potential sweep rate of 5 mV s−1. After Recio *et al*. [30].

**1830 1850 1860 1910 1920 1930 1940 1950 1960 1975 2020**

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Faraday’s laws of electrolysis

Bird nickel deposition on Pt

Shore nickel nitrate bath patent

Bottger nickel and ammonium sulfate bath

Remington ammonium chloride based Ni bath and Ni pellet anodes

Adams ammonium nickel sulfate commercial Ni bath patent

**Watts optimised Ni bath bath**

Schlotter bright ‘Watts’ Ni bath

Cambi and Piontelli nickel sulfamate bath patent

DuRose semi-bright Ni bath

Watson & Edwards levelling and brightening studies

Modified Watt’s Ni baths for composite plating

Superhydrophobic, self-cleaning coatings

Self-lubricating, layered inclusion composite Ni (and Co) coatings

Nanostructured Ni deposits in rectangular channel flow

.

**Figure 1.**

**Figure 2.**

**Electrodeposition conditions**

* Cell/electrode geometry
* Current density
* Temperature
* Potentiostatic/galvanostatic
* Steady or pulsed current
* Bath agitation
* Electrode movement

**Electrical control**

* Potentiostatic
* Constant current
* Steady d.c.
* Pulsed waveform

**Electrolyte composition**

* Metal ions
* Complexants
* pH
* Conductive salts
* Additives

**Particle dispersion**

* Stability
* Setting time
* Agitation

**Electrolyte type**

* Aqueous
* Ionic liquid
* Number of phases
* Agitation

**Deposit properties**

* Elemental composition
* Surface morphology
* Composition of phase(s)
* Electrical conductivity
* Tribological properties
* Surface roughness

**Direct current**

**power supply**

**Anode**

**Cathode**

**Substrate**

 Pre-treatment

 Conductivity

 Roughness

 Movement

**Flow conditions**

 Laminar/turbulent

 Stirrer type/size

 Stirrer position

 Stirrer speed

**Figure 3.**



**10 g dm-3**

**7 g dm-3**

**3 g dm-3**

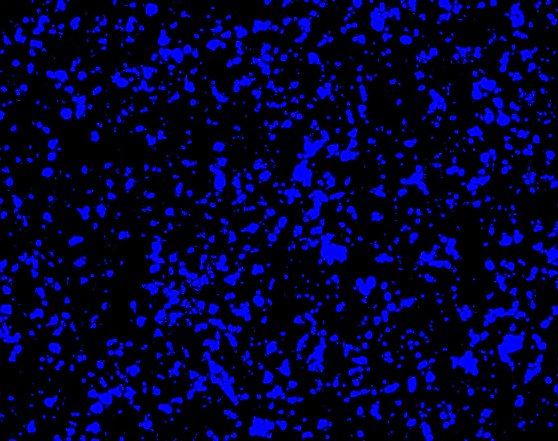
**Time / s**

**Figure 4.**

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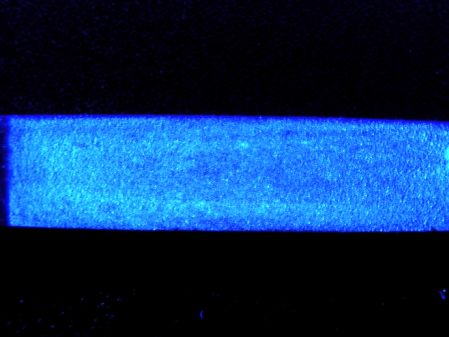
**% WS2 content of coating**

**Figure 5.**



**100 µm**

**(b)**



**1 cm**

**(a)**



**(c)**

**Intensity / arbitrary units**

**Wavelength / nm**

**Figure 6.**



**Figure 7.**