Electrodeposition of compositionally modulated tin-cobalt alloy multilayer coatings as plain bearing overlays

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ELECTRODEPOSITION OF COMPOSITIONALLY MODULATED TIN-COBALT ALLOY MULTILAYER COATINGS AS PLAIN BEARING OVERLAYS

by

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SYNOPSIS

Lead-based alloy electrodeposits have been used as overlays for plain bearings for many years. The toxicity of lead has not been a problem for the industry until recently with the initiation of the End-of-Life Vehicle (ELV) directive in the European Union. This legislation requires the member states to phase out lead in the future, thus promoting a search for lead-free alternatives. The aim of this research was to investigate the electrodeposition and the fatigue properties of compositionally modulated Sn-Co alloy multilayer coatings as possible overlays for plain bearings.

Following a comprehensive review on the electrodeposition of Sn-Co alloys, a novel sulfate/gluconate electrolyte was established, from which compositionally modulated multilayer coatings can be deposited by varying the applied current density only, i.e. pure tin coatings were deposited at current densities lower than the limiting current density for the deposition of tin, whilst Sn-Co alloy coatings were deposited at much higher current densities. It was found that the pH value of the solution was crucial to maintain the desired deposit composition/current density relationship, with pH 3.5-4 being the optimum range. The main function of sodium gluconate was to inhibit the hydrolysis of tin(II) ions. The total concentration of tin(II) ions in the electrolyte and the agitation strength were the two factors which were employed to markedly increase the limiting current density for the deposition of tin, leading to an increased overall deposition rate for coatings. It was also found that the addition of boric acid and a non-ionic surfactant, Tween 20, to the solution was essential for the deposition of satisfactory Sn-Co alloy coatings.

The electrodeposition of Sn-Co alloys was also carried out using pulsed current, in order to enhance the electrocrystallisation process and thus prevent the formation of dendritic coatings. Compositional analysis indicated that Sn-Co alloy coatings obtained under pulsed current conditions had more uniform cobalt content within a wide current density range of 1-4 A/dm² than under direct current conditions. After ruling out the selective dissolution of cobalt during the off-time by AES depth profiling, the effect of pulsed current parameters on the deposit composition was explained on the basis of the mass transport theory derived from Ibl's duplex diffusion layer model for pulse electroplating, leading to the conclusion
that pulsed current was able to slow down the deposition rate of the more noble component of an alloy by controlling the mass transport in the non-stationary diffusion layer.

Potentiodynamic polarisation studies confirmed that the deposition of Sn-Co alloys from the new sulfate/gluconate bath forms a regular alloy codeposition system. The cobalt was codeposited only after the applied current density had exceeded the limiting current density for the deposition of tin. Tween 20 exhibited a selective suppression effect on the deposition process of tin but had negligible effect on cobalt. Boric acid was found to intensify the suppression effect of Tween 20 and shift the effective deposition potentials in the positive direction. The effect of Tween 20 was explained by its potential-dependent adsorption on the electrode surface.

Compositionally modulated Sn-Co alloy multilayer coatings with distinct and continuous interfaces were successfully deposited on the surface of plain bearings. The fatigue strength values of these coatings fell in the range of 60-90 MPa. The resistance to the nucleation of fatigue cracks in the multilayered overlay was found to be dependent more on the cobalt content in the electrolyte (or the magnitude of the composition modulation between the neighbouring layers), rather than the thickness configuration of individual layers or the residual internal stress in the coatings. SEM examination of the cross-section of plain bearings revealed that the fatigue cracks may be deflected at the interfaces on reaching the hard layers of Sn-Co alloys, causing the cracks to travel greater distances and consume more energy.

Keywords: electrodeposition, compositionally modulated multilayer (CMM) coatings, tin alloys, lead-free, plain bearings, overlay, fatigue strength, pulsed current
I wish to express my sincere gratitude to my supervisors, Dr. G. D. Wilcox and Prof. D. R. Gabe for their guidance and constant encouragement throughout the course of the research programme.

I would also like to express my gratitude to Dana Glacier Vandervell Bearings Co. Ltd. and ORS Award for providing the financial support to this project. Thanks are also due to Dr. C. P. S. Johal, Dr. P. Detassis and Mr. J. Carey, for their invaluable advice and assistance on the design and fatigue tests of the new plain bearing overlays.

In addition, much is owed to my colleagues and the technical staff within the department for their support

Keming Chen
March 2004
Dedicated to my wife Hui
and son Zhangqu for their love and patience
Table of Notation

**Symbols**

- **A**: Area, dm²
- **Co, b**: Concentration of species in bulk electrolyte, mol/I
- **CSO**: Concentration at electrode surface under direct current conditions
- **CS1**: Concentration at electrode surface at the end of off-time, mol/I
- **CS2**: Concentration at electrode surface at the end of on-time, mol/I
- **Cm**: Average of surface concentrations (CS1, CS2) during pulse plating
- **D**: Diffusion coefficient, cm²/s
- **E**: Electrode potential, V; or Young's modulus of elasticity in Equation 6.5, MPa
- **E°**: Standard electrode potential, V
- **f**: Frequency, Hz
- **F**: Faraday's constant, 96485 C/mol
- **j**: Current density, A/dm²
- **j0**: Exchange current density, A/dm²
- **jlim**: Limiting current density, A/dm²
- **jm**: Average current density, A/dm²
- **jp**: Peak current density, A/dm²
- **jPL**: Pulse limiting current density, A/dm²
- **jPL***: Dimensionless pulse limiting current density defined as \( j_{PL} / j_{lim} \)
- **I**: Current, A
- **J**: Diffusion flux, mol cm⁻² s⁻¹
- **L**: Characteristic length
- **M**: Molar mass, or atomic weight of elements, g/mol
- **n**: Number of electrons involved in electrochemical reaction
- **R**: Gas constant, 8.314 J mol⁻¹ K⁻¹
- **t**: Time, or deposit thickness
\( t_{c, d} \) Charging or discharging time of double layer
\( t_{\text{on, off}} \) Pulse on or off-time,
\( T \) Thickness, or temperature, or Pulse period equal to \( t_{\text{on}} + t_{\text{off}} \)
\( W_a \) Wagner’s number
\( x \) Distance from the cathode
\( X_{Co} \) Molar fraction of cobalt in tin-cobalt alloys

**Greek**
\( \alpha \) Activity of metal ions
\( \delta \) Diffusion layer thickness,
\( \epsilon \) Deflection of the free end of copper strip
\( \varepsilon \) Cathodic current efficiency, %
\( \eta \) Overpotential, V
\( \frac{d\eta}{dj} \) Slope of polarisation curve
\( \kappa \) Conductivity, S/cm
\( \nu \) Nucleation rate
\( \theta \) Duty cycle, %
\( \rho \) Density, g/cm\(^3\)
\( \sigma \) Internal stress, MPa
\( \tau \) Transition time
\( \tau^* \) Dimensionless transition time

**Abbreviations**
AES Auger Electron Spectroscopy
CCE Cathodic current efficiency for metal deposition
CMA Compositionally modulated alloys
CMM Compositionally modulated multilayer
DBT Dual bath technique
DC/PC Direct current/Pulsed current
EDX Energy Dispersive X-ray spectroscopy
FEG-SEM Field Emission Gun Scanning Electron Microscope
SBT Single bath technique
SCE  Saturated Calomel Electrode (+0.242mV with respect to the standard hydrogen electrode at 25°C)

SEM  Scanning Electron Microscope
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1 INTRODUCTION

1.1 Overlays for plain bearings

Plain bearings are important components designed to operate in conjunction with rotating journals such as those in automotive engines. The main purpose of using bearings is to minimise or eliminate the wear and minimise the friction between the two surfaces that are in relative motion. Modern lubricated plain bearings usually utilise a strong steel backing to which is bonded a softer bearing lining material. The most common lining materials in current use are copper-lead, lead-bronze and aluminium-tin alloys, whereas the traditional bearing linings are the tin-based or lead-based white-metals (Babbitts) [1]. Copper-lead and lead-bronze linings have sufficiently high load-carrying capacity, however, they are deficient in a few respects, e.g. bearing seizure and high rate of journal wear, especially in the early stage of running. They are also prone to corrosion attack by the oxidised lubricating oils which are acidic. It is these limitations that necessitate the application of overlays – a thin electrodeposited layer of lead-based alloys, about 25 μm thick, which provides the actual surface with good bearing properties.

Three typical overlay alloys in common use are lead-tin, lead-tin-copper and lead-indium. The success of these soft overlays are mainly due to their superior compatibility with the mating surfaces and their improved corrosion resistance. Moreover, they are able to conform to small misalignment in the bearing assembly so distributing the imposed loading over a greater effective area and lowering the peak stress experienced by the bearing. They also have the ability to adsorb and embed particles of dirt from the lubricant. Although the use of overlay coatings was originally initiated by the problems associated with the hard copper-lead and lead-bronze linings, they have now been used on the whole range of bearing linings for improved tribological performances.
1.2 Environmental trend of lead elimination

No general problems of any significance existed with the use of lead-based overlays, other than its level of toxicity. Lead ranks second, just behind arsenic, on the CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) priority list of Hazardous Substances [2] published by the Agency for Toxic substances and Disease Registry (ATSDR) and the Environmental Protection Agency (EPA). The systemic toxic effects of lead in humans have been well-documented. Brain damage, kidney damage, and gastrointestinal distress are seen from short-term exposure to high levels of lead. Long-term exposure results in effects on the blood, central nervous system, blood pressure, kidneys, and Vitamin D metabolism.

Most recently, environmental issues are becoming a growing concern around the world. Some developed countries have taken regulatory actions to eliminate or impose strict management requirements on the use of lead. In Europe, a draft directive [3] proposes lead be phased out of new electrical and electronic equipment (EEE) and move towards lead-free processes and materials throughout the electronics industry by 2008, in particular lead in solders, due to the concerns about lead leaching out of old electronic equipment into water supplies and the resulting damage to the eco-system. In Japan, many major companies, for example, NTT, Hitachi, Matsushita, and Fujitsu, have taken up the challenge and have announced measures and timescales to reduce or completely eliminate lead from some or all of their products. These activities in European and Japanese companies have caught the attention of industry world-wide and the interest in lead-free solder alternatives is increasing dramatically.

In the automotive industry, there is a separate European Union (EU) directive applicable, i.e. the End-of-Life Vehicle (ELV) Directive [4]. It requires the member states ensure that materials and components of vehicles put on the market after 1 July 2003 do not contain lead and other hazardous substances such as mercury, cadmium and hexavalent chromium, other than in cases where exemption is applicable. Although at present lead-bronze bearings are on the exemption list, however, according to Article 4.2 (b) of the directive, the European Commission shall amend the list on a regular basis in order to delete
CHAPTER 1 INTRODUCTION

materials and components of vehicles from the exemption if the use of these substances is avoidable. Therefore, whether lead will be phased out of the manufacture of plain bearings or not in the future depends on technical and scientific progress. Once the first lead-free product is marketed, elimination of lead from plain bearing applications will be legislated and the consequent impact on the whole bearing industry will be far reaching.

From the pressures of legislation, commercial competition, and public sentiment as well, the trend to eliminate the use of lead is increasing and shows no sign of subsiding. Consequently various sectors of industry are considering their strategy for minimising or eliminating lead usage. The objective of this research is to identify alternative lead-free electrodeposits for the traditional lead-based alloy overlays on plain bearings for automotive engines. The substitutive alloy needs to possess good surface properties required by the overlay, while the choice of the alloy elements and the electrolyte should not introduce any significant new environmental risk or health hazards.

1.3 Lead-free alternatives for conventional overlays

From the viewpoint of the tribological function of an overlay, it is a prerequisite that any potential lead-free alternatives for conventional lead-based overlays must be soft, namely they must have low shear strength. Table 1.1 summaries the hardness, shear strength and the melting point of some soft metallic coatings [5], including lead. Although thallium and cadmium have comparable physical properties to lead, both of them are toxic. On the other hand, silver and gold are precious metals. Any advantages that they possess will be largely offset by their high cost, particularly for the large volume production market, and thus their use has been mainly confined to speciality bearing applications such as in the aerospace industry. Indium has been used only with lead as the overlay material in the past. Amongst all these soft metals, tin is probably the most practical and the most appropriate alternative to lead, as tin is not only comparable with lead in bearing properties, but is also non-toxic and cheap. Meanwhile, the electrodeposition of tin and tin-based alloys are established surface finishing processes. Therefore, it can be envisaged that the development of lead-free alternatives for conventional lead-based overlays will be centred around tin and tin-based alloys.
Table 1.1 Physical properties of some soft metal coatings [5]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Hardness</th>
<th>Shear strength</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moh</td>
<td>kg/mm²</td>
<td>°C</td>
</tr>
<tr>
<td>In</td>
<td>1</td>
<td>0.75</td>
<td>155</td>
</tr>
<tr>
<td>Tl</td>
<td>1.2</td>
<td>1.12</td>
<td>304</td>
</tr>
<tr>
<td>Pb</td>
<td>1.5</td>
<td>0.68</td>
<td>328</td>
</tr>
<tr>
<td>Sn</td>
<td>1.8</td>
<td>0.77</td>
<td>232</td>
</tr>
<tr>
<td>Cd</td>
<td>2</td>
<td>1.9</td>
<td>321</td>
</tr>
<tr>
<td>Au</td>
<td>2.5</td>
<td>4.5</td>
<td>1063</td>
</tr>
<tr>
<td>Ag</td>
<td>2.5-3</td>
<td>4.7</td>
<td>961</td>
</tr>
</tbody>
</table>

However, the traditional tin and tin-based alloy electrodeposits are not sufficient as a substitute for lead-based overlays on plain bearings, as they do not have the required fatigue strength, leading to cracking under arduous applications. Some further modification must, therefore, be carried out. One possible approach proposed in this research is to strengthen the tin-based overlay through the electrodeposition of compositionally modulated multilayer (CMM) coatings with alternating hard layers of tin-based alloys and soft layers of pure tin, each of which are one or a few microns thick. The concept of layering two materials of different properties has been employed to produce new alloys with unique and outstanding properties, which are not obtainable from their parent constituents. So far there is little evidence that any attempt has been made to electrodeposit multialyered overlays on plain bearings.

1.4 Scope of this research

This research has concentrated on electrodeposition using a single electrolyte, and the fatigue strength assessment of the compositionally modulated Sn-Co alloy multilayer coatings as potential overlays for plain bearings. The desired structure is illustrated in Figure 1.1. In such a coating system, individual layers of different compositions and thicknesses are built up alternately up to an overall thickness of 13-16 microns. The cobalt
content in the Sn-Co alloy layers was thought to be desirable at around 20 wt.%. The actual optimum value was achieved by examining the effects on property enhancement. The pure tin layer was always deposited as the top layer providing good surface properties. As one single electrolyte was preferred by the industry for the electrodeposition of these multilayered coatings, the composition modulation was realised mainly by varying the applied current density.

Prior to embarking on experimental work, a literature review was conducted to obtain the background information relating to the structure and materials of plain bearings and overlays, the electrodeposition of Sn-Co alloys, pulsed electroplating, and finally compositionally modulated multilayer coatings. The review on the electrodeposition of Sn-Co alloys centres around the chemistry of the electrolyte, including the complexing of tin and cobalt ions and the oxidation of tin ions from tin(II) to tin(IV), together with the properties of Sn-Co alloy electrodeposits. The theory of pulse electroplating is reviewed as pulsed current was employed in this research to avoid the formation of dendritic deposits of Sn-Co alloys. The review on compositionally modulated multilayer coatings is primarily concerned with the characteristics and requirements of two different methods, i.e. the dual bath technique and the single bath technique, for the electrodeposition of multilayer coatings. The property enhancement, mainly the fatigue strength and the corrosion resistance of multilayered coatings, has also been reviewed.

The experimental research was initially focused on the development of a new electrolyte, which had the potential for the electrodeposition of multilayer coatings, namely one from which satisfactory deposits of both pure tin and Sn-Co alloys could be achieved by changing the applied current density. The influence of various parameters including the electrolyte formulation and the operating conditions, such as temperature and agitation, on the deposition characteristics of Sn-Co alloys from the new sulfate/gluconate electrolyte were investigated systematically to achieve the optimum conditions. Following the study under direct current conditions, pulsed current was employed to eliminate the formation of dendritic Sn-Co alloy deposits during prolonged electroplating. A detailed study of the effect of pulsed current parameters on the deposit morphology, composition and the cathodic current efficiency was conducted and the results compared against those obtained using direct current.
CHAPTER 1 INTRODUCTION

The electrodeposition of compositionally modulated Sn-Co alloy multilayer coatings was conducted first on copper substrates and later on actual plain bearings. The multilayered structure was confirmed through the SEM examination of sample cross-sections. The influences of the thickness configuration of individual layers and the current waveforms for the deposition of Sn-Co alloy sublayers on the deposit morphology and the internal stress were studied. The results of primary fatigue tests on plain bearings with electrodeposited Sn-Co alloy multilayer overlays has also been reported.

Cathodic potentiodynamic polarisation studies were conducted to understand the codeposition mechanism of Sn-Co alloys and the effect of a non-ionic surfactant—Tween 20. Titration experiments were carried out to study the effect of electrolyte constituents including sodium gluconate, the complexing agent, and boric acid on the hydrolysis of tin(II) ions in the solution.

The main discussion of the results consists of the codeposition mechanism of Sn-Co alloys, the main function of sodium gluconate, the characteristics of mass transport and electrocrystallisation during the pulsed current electrodeposition of Sn-Co alloys, as well the adsorption of Tween 20 and its selective suppression on the deposition of tin. The factors which govern the fatigue strength of multilayered Sn-Co alloy overlays have also been discussed, and form the foundation of the suggestions for further work.
2 PLAIN BEARINGS AND OVERLAY COATINGS

2.1 Introduction

A type of bearing is required whenever a load is transmitted between surfaces moving relatively in any mechanism or machines. The essential function of a bearing is to locate and guide the moving members, to improve the tribological behaviour and thereby increase the operational life of the components, and to minimise the loss of energy resulting from the friction under the applied loadings.

Plain bearings (as shown in Figure 2.1) may be defined as those in which the relative motion between the mating surfaces is sliding in contrast to rolling contact as in ball, needle and roller bearings. The total bearing assembly consists of the housing, the bearing, the lubricant, if any, and the mating surface be it shaft, pivot, slide-way or thrust collar. Plain bearings are more commonly used for automotive engines. They can be designed to carry either a transverse, or an axial or thrust load, or a combination of both. Depending on the load pattern, rotation speed, and lubricant viscosity and supply, a plain bearing might operate under fully hydrodynamic lubrication, or boundary lubrication, or no lubrication conditions. For different working conditions, specific bearing design considerations should be given.

2.2 Design of plain bearings

The tribological properties of a plain bearing require the materials involved to possess [6]:

- Ability to retain a lubricant.
- Compatibility, to avoid "cold welding".
- Conformability, to compensate for imperfections in shaft geometry.
- Embeddability, to absorb dirt and debris carried by the lubricant.
CHAPTER 2  PLAIN BEARINGS AND OVERLAY COATINGS

- High strength, to resist deformation by both steady and fluctuating loads.
- Corrosion and wear resistance.
- Good thermal conductivity.

Of these properties, the load carrying capacity and the wear resistance are the characteristics of a hard phase, while the compatibility, the conformability, and the embeddability can only be conferred by a soft phase. These properties are mutually conflicting and exclusive, so it is difficult to achieve these requirements in a single material. A balance or compromise dictated by the application is often necessary.

In practice, one way of compromise is electroplating a thin and soft layer, called overlay, onto the surface of the harder bearing materials, such as copper-lead and aluminium alloys. The overlay functions to conform to small errors of alignment in the bearing assembly, and to absorb foreign debris particles. The overlay could also serve to protect the bearing alloy from corrosion attack by oxidised lubricating oils. When using an overlay, the effective fatigue strength of the bearing could be apparently increased although fatigue of the overlay occurs at lower loads than that for the bearing lining [7].

In general, a plain bearing consists of a strong backing metal for support, a hard bearing alloy lining to withstand the loads, and an overlay on the running surface to provide the bearing with certain surface properties (Figure 2.2). In most cases, an interlayer or a barrier, typically nickel, is also applied between the lining and the overlay either to prevent the interface diffusion of tin in lead-bronze bearings [7, 8], or to overcome the difficulties in overlay electroplating of aluminium bearings [9]. However, as this interlayer may undermine the performance of engine bearings when exposed to the mating surface, attempts are ongoing to eliminate this necessity.

2.3 Overlay materials

2.3.1 Conventional lead-based alloys

An overlay is traditionally produced from a lead-based alloy containing alloying elements such as tin, indium, and/or copper. Tin is added chiefly to provide some corrosion resistance and copper is added chiefly to improve the wear resistance of the lead-tin. An
alternative to tin is indium, which also provides the lead with corrosion resistance while maintaining good surface properties.

The most common lead-based overlay alloys are PbIn8, PbSn10, and PbSn10Cu2. Of these three alloys, PbIn8 has superior fatigue strength but poor wear resistance. PbSn10Cu2 lacks the fatigue strength of PbIn8, but has the best wear resistance [8]. PbSn10 offers a good compromise of properties. There also exist some variants such as PbSnIn [10] and PbSnCuIn [11], which have high melting temperatures and provide superior sliding properties under high speed service conditions.

2.3.2 New overlay materials

The service environment of a bearing has become more and more severe and conventional overlay alloys can no longer meet the requirements of being operated at higher temperatures, under higher loads, and over longer periods of time. To overcome these problems, a number of new materials have been developed.

2.3.2.1 Composite materials

In recent years, the growing use of cast-iron crankshafts which are inherently very abrasive in nature, lead to the development of composite overlays of lead-tin-alumina [12], in which the hard particle phase of alumina is dispersed in the soft lead-tin alloy matrix. The addition of the hard particles considerably improves the wear resistance of the overlay, while the soft matrix ensures that the desirable conformability and embeddability is retained. Another composite overlay consists of a soft metal (selected from zinc, copper, tin, lead, antimony, indium, silver and alloys thereof) matrix and dispersed amorphous carbon [13]. It is claimed that the addition of amorphous carbon eliminates the need for the nickel interlayer which can lead to problems with scuffing and seizure of the bearing when it is exposed to the mating surface.

2.3.2.2 Two-phase alloys

A two-phase alloy comprises of a matrix of aluminium, copper, or silver, and an embedded metal phase which is softer than the matrix and also insoluble in the matrix, e.g. tin, or lead. The soft constituent of an overlay alloy is usually present in a concentration which
decreases along a concentration gradient perpendicular to the effective surface of the overlay as the distance from the effective surface increases. The matrix phase provides superior mechanical strength over conventional lead-based alloys while the high concentration of the soft phase confers good sliding properties.

The aluminium-(10-50%) tin two-phase alloy [14] is a typical one and is used with cast lead-bronze for the most arduous long life applications. Aluminium cannot be electrodeposited easily, so sputtering is used as an alternative method of manufacture.

2.3.2.3 Zinc-based alloy
An alloy of zinc [15] with 0.5 to 25% by weight of a metal selected from nickel, cobalt and iron was reported to have greatly increased wear resistance and high temperature capacity (above 250°C). Besides the zinc-based alloy, zinc was also introduced into a lead-based overlay alloy to enhance corrosion resistance and conformability of the bearing alloy layer [16].

2.3.2.4 Tin-cobalt alloy by brush electroplating
By brush electroplating, a tin-cobalt alloy [17] of preferred range from 2 to 8 weight percent of cobalt was produced from a sulfate/heptonate solution. This alloy was found to possess fatigue strength and metallurgical stability in excess of other known overlay alloys whilst maintaining the desirable properties of conformability and debris embeddability. Far from the overlay becoming depleted in cobalt the distribution of cobalt within the tin matrix actually becomes more homogeneous. The tin-cobalt alloy seems quite promising as a lead-free overlay alloy.

2.3.2.5 New interlayer
The electrodeposition of a nickel diffusion barrier between the bearing lining and the overlay is a widely accepted practice. This offers some relief, but nickel has undesirable seizure characteristics. An alternative diffusion barrier based on amorphous Ni-P alloy [18] has been identified through which the extent of diffusion of tin was markedly reduced.
2.4 Properties of overlays

2.4.1 Geometrical size

The overlay thickness in bearing design is vital to its performance as fatigue life diminishes markedly with increasing thickness [19], while the conformability and embeddability will be impaired if the thickness is decreased beyond the dirt particle’s size. Overlays that are too thin also have a short service life. The gross loss of the overlay is no longer acceptable, although the danger of seizure is greatest during the initial running-in period. The overlay of a plain bearing is expected to last the whole lifetime of the bearing. In practice, the overlay thickness does not usually exceed 50 μm, the thickness depending on application.

2.4.2 Hardness

The hardness of the as-plated overlays is usually less than 20 HV [20]. For an overlay of lead-tin or lead-tin-copper alloy, its hardness falls with prolonged operation time under high temperature, because these alloys are metallurgically unstable and tin will diffuse from the overlay. This softening of the overlay, as might be expected, would favour the conformability and embeddability but put both fatigue strength and wear resistance at a disadvantage.

2.4.3 Fatigue strength

Fatigue failure of an overlay takes place when it is subjected to excessive alternating loading caused by factors such as lugging an engine at low speed under high load, overfueling and detonation. It could also result from localised concentration of load due to misalignment as in the case of edge loading, bent rod, tapered or barrel shaped housing or journal. Fatigue damage is readily distinguished from other failure mechanisms. In fatigue failures the cracks start at the bearing surface, propagate normal to the surface until they approach the interface between the overlay and the bearing alloy layer or the nickel barrier if applied, then turn through 90° and extend parallel to the interface leaving a thin layer of
Overlay attached to the shell [21]. A typical example of overlay fatigue is shown in Figure 2.3. On the surface of a fatigued overlay, there forms a network of fine cracks vertical to the rotation direction of the journal, or fatigue pits due to the separation and loss of pieces of overlay material as the neighbouring fatigue cracks join up.

Comparison of the fatigue strength of the three major overlays at the same thickness shows that lead-indium is about 20 percent stronger than the lead-tin-copper, while lead-tin and lead-tin-copper have similar fatigue strengths [20]. Besides the composition dependence, another important characteristic of fatigue strength is that it depends on the overlay thickness [1, 6-7]. As shown in Figure 2.4, the fatigue strength of the conventional lead-tin, lead-tin-copper, and lead-indium overlay increases rapidly as their thicknesses are decreased. However, too thin overlays, as stated previously, have too short a life. Therefore, most overlay thicknesses are specified in the range of 12 to 25 microns. In addition, adequate pre-treatment must be conducted before the overlay is deposited on the surface of plain bearings. Otherwise, the fatigue strength of the overlay will be markedly decreased.

2.4.4 Wear resistance

The principal causes of wear of the mating surfaces are adhesion and abrasion. The welding and subsequent shearing of the mating surface asperities leads to adhesion. Either a rough harder surface sliding against the softer surface or rough hard particles in the lubricants trapped between the sliding surfaces cause abrasion.

An overlay is often abraded and worn by hard foreign particles carried by the lubricant oil, which are too large to embed in the overlay. For this reason, wear resistance of the overlay for heavy fuel engine bearings is a property of primary importance. In the environment of such overlays there present numerous relatively small black particles, which contain sulphur and calcium and are associated with the products of relevant lubricating oil additives or of the heavy fuel combustion, or both [9]. These particles may lead to rapid removal of the overlay. Excessive wear of overlays may also happen in bearings mating with nodular cast iron crankshafts [8].
2.4.5 Corrosion resistance

Two factors lead to the corrosion and subsequent degradation of a bearing overlay. First of all, during service of a bearing, the lubricant becomes corrosive due to the breakdown of inhibitors and the water from the reaction of the long chain fatty acid “extreme pressure” additives at the operating temperature. For example, corrosion is a major problem for the bearing overlay in medium-speed diesel engine where residual fuels and degraded oils are used [9].

Secondly, the diffusion of alloying elements from the overlay makes it liable to corrosion. Corrosion resistance of a bearing overlay was postulated to be in part due to the presence of either tin or indium oxide at the alloy surface [22]. Therefore diffusion to the surface of either of these two elements is critical to ensure a reduced corrosion rate. Alloys with a concentration of these elements below the threshold limit appear to be unable to sustain a continuous oxide film on the surface and hence corrosion resistance decreases. Wilson and Shone [22] reported the threshold limits of the 3-4 wt.% tin in lead-tin or lead-tin-copper alloy and about 5 wt.% indium in lead-indium alloy are required for acceptable corrosion resistance.

2.5 Electrodeposition of overlay for bearings

Overlays can be produced by casting, electroplating, or a physical vapour deposition (PVD) method, such as sputtering. The grains of an overlay produced by the casting method are usually coarse, while the PVD method is more expensive and sophisticated than electroplating. The PVD method is only applied when the overlay contains alloying elements, e.g. aluminium, which cannot be electrodeposited easily, although it features a much wider material range [23-24] and easier composition and thickness control than the electrodeposition method.

Electrodeposition of overlays has been a recognised technique for a long time in the manufacture of plain bearings for its low investment cost, simple equipment requirements,
room temperature operation, and mass production possibility. The major drawback of 
electroplating involves the subsequent disposal of effluent which otherwise causes 
potential pollution to the environment. In practice, the lead-tin and lead-tin-copper 
overlays are produced by codeposition of lead, tin, and/or copper from a single solution, 
whilst the lead and indium are deposited separately and then alloyed together by a 
subsequent heat treatment. Table 2.1 gives the operating conditions for electrodeposition of 
the traditional lead-based overlay alloys.

2.6 Future of overlay alloy electrodeposition

As a result of its advantages over other deposition techniques, electrodeposition will 
continue to dominate the manufacture of overlay coatings for bearings in the near future. 
To strengthen the competitiveness, conventional electroplating processes need to be further 
modified, particularly with the purpose of developing new alloy systems and eliminating 
the use of hazardous substances so as to conform the global environmental protection laws.

Commonly used materials known to have desirable bearing properties include lead, tin, 
indium, antimony, bismuth, silver and potentially cadmium, thallium, and alloys of these 
metals. In 1980s, electrodeposition of thallium [29], lead-thallium [30], and lead-
cadmium [31-32] were studied and optimised in the context of the useful tribological 
characteristics. However, due to the marked acute toxicity of cadmium and thallium, these 
materials receive less investigation. As can be expected, these materials will definitely be 
ruled out of any future development. For antimony, bismuth, and indium, they are mainly 
added as the auxiliary alloying elements to increase the strength and/or corrosion resistance 
of the lead matrix. They have never been used individually or even as an alloy matrix. The 
disadvantage of silver is that it is relatively expensive.

The future development of new overlay alloy systems is expected to be mainly based on tin 
and tin-based alloys. For its low melting point, softness and malleability in the manner of 
lead, tin has shown importance in the manufacture of bearings. Tin has been used 
individually as a sacrificial overlay coating, e.g. on aluminium-based alloys, and showed 
good anti-seizure properties [33]. Tin-based alloys also form an independent category of 
bearing alloys. Nevertheless, in comparison to the toxicity of lead, tin is a completely eco-
Table 2.1 Electrodeposition conditions for traditional overlay alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSn</td>
<td>Fluoroborate bath: Lead (fluoroborate) 200 g/l Stannous tin (fluoroborate) 20 g/l Free fluoboric acid 50 g/l An addition agent (gelatine, peptone, resorcinol or hydroquinone) 5 g/l Room temperature Cathode current density 10 A/dm²</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>Sulfamate bath: Lead 49 g/l Tin 5.5 g/l Peptone, gelatine, pyrogallol 2.5 g/l pH 1.2 Room temperature Current density 0.5 A/dm²</td>
<td>[25]</td>
</tr>
<tr>
<td>PbSnCu</td>
<td>Lead fluoroborate 150–200 g/l Tin fluoroborate 5<del>15 g/l Copper fluoroborate 1</del>3 g/l Gelatine 2 g/l Hydroquinone 2 g/l</td>
<td>[26]</td>
</tr>
<tr>
<td>PbIn</td>
<td>Lead electroplating: Lead fluoroborate 440 g/l (Lead) 240 g/l Free fluoboric acid 60 g/l Free boric acid 27 g/l Animal glue 0.2 g/l or peptone 0.2<del>1.0 g/l Temperature 25</del>40°C Cathode current density 5~7 A/dm²</td>
<td>[27-28]</td>
</tr>
<tr>
<td></td>
<td>Indium electroplating: Indium sulfamate 40<del>120 g/l Sulfamic acid 10</del>60 g/l NaCl 15<del>100 g/l Dextrose 2</del>25 g/l Triethanolamine 1<del>5 g/l Sodium sulfamate 70</del>320 g/l Liquid temperature 10<del>50°C Current density 1</del>10 A/dm² pH 3.8 or less</td>
<td></td>
</tr>
</tbody>
</table>
friendly metal. Therefore, it is going to be a natural tendency that tin and its alloy will play an increasingly important role in the future of eliminating lead from overlay alloys, due to its tribological characteristics and environmental adaptability.

The possible tin-based alloys include tin-nickel, tin-zinc, tin-manganese, and tin-cobalt. A feasibility study by Dana Glacier Ltd. indicated that tin-nickel alloy did not have sufficient corrosion resistance. The tribological properties of tin-zinc and tin-manganese alloy are not known yet. The most promising alloy should be tin-cobalt, which has already been brush plated as an overlay [17]. The investigations reported in this thesis have concentrated on the electrodeposition of tin-cobalt alloys.
3 Tin-cobalt alloys

3.1 Introduction

The electrodeposition of tin-cobalt alloys was stimulated by the successful co-deposition of tin and nickel, because cobalt and nickel have close chemical and metallurgical similarities. The first patent on tin-cobalt alloy electrodeposition, from an alkaline cyanide electrolyte, was published in 1939. However, the deposit contained only 0.35% cobalt. Deposits containing greater amounts of cobalt were later obtained from acidic fluoride electrolytes (about 30% cobalt) in 1951 [34] and alkaline pyrophosphate solutions (up to 87% cobalt) in 1960 [35]. These baths were of scientific interest only, and none of them achieved commercial importance. It was not until the 1970s that an increasing interest in the electrodeposition of tin-cobalt alloys was again. All of the above-mentioned baths were re-examined. New baths, including sulfate/gluconate [36-38], fluoroborate [39], and tartarate solutions [40], were established. The main drive behind this development was that tin-cobalt alloy deposits with a thickness of less than 2 μm could produce a colour very similar to that of decorative chromium coatings, without much of the inconvenience or environmental problems that accompany chromium electroplating. As an environmentally acceptable alternative to chromium coatings, tin-cobalt alloy electrodeposits were applied and extensively explored in both the 1980s and 1990s.

According to the chemical characteristics of the constituents, the electrolytes reported for the electrodeposition of tin-cobalt alloys can be broadly divided into the following three categories:

- Sulfate/gluconate bath
- Fluoride bath
- Pyrophosphate bath

The sulfate/gluconate bath is highly prone to oxidation. The fluoride bath is hazardous in that it contains high concentrations of fluorides at low pH values, necessitating the use of...
special equipment for containing, heating, filtering, and pumping the electrolyte. The pyrophosphate bath is relatively the least studied. Of these, proprietary solutions of sulfate/gluconate and fluoride are currently available.

3.2 Sulfate/gluconate bath

3.2.1 Solution make-up

A typical sulfate/gluconate electrolyte, called Achorlyte, is covered by a US patent [41]. Further details of this process were later reported by Hemsley and Roper [37]. Recently, research on electrodeposition of tin-cobalt alloys from sulfate/gluconate baths has been systematically addressed [42-44]. As listed in Table 3.1, the striking feature of the sulfate/gluconate bath, is that the metal content in the solution is very low. Therefore, this bath is suitable primarily for the deposition of thin coatings and can be simply discarded after being used to exhaustion.

3.2.2 Gluconate complexes

In the sulfate/gluconate bath, sodium gluconate was added as a complexing agent for the metal ions of Sn(II) and Co(II). Gluconate is designated as $\text{GH}_4^-$, and the corresponding acid is gluconic acid, i.e. $\text{HGH}_4$, where the first $\text{H}$ refers to the carboxylic acid hydrogen and $\text{H}_4$ refers to the four hydrogens on the secondary alcohols.

\[
\begin{array}{c}
\text{COOH} \\
\alpha \quad \text{HCOH} \\
\beta \quad \text{HOCH} \\
\gamma \quad \text{HCOH} \\
\delta \quad \text{HCOH} \\
\text{H}_2\text{COH} \\
\text{HGOH}
\end{array}
\quad
\begin{array}{c}
\text{COO}^- \\
\text{HCOH} \\
\text{HOCH} \\
\text{HCOH} \\
\text{HCOH} \\
\text{H}_4\text{COH} \\
\text{GH}_4^-
\end{array}
\]

Gluconic acid forms two kinds of complexes [45]. In acid media, the metal ion is bound into a complex via a carboxyl group ligand. The stability constants have relatively small values. In alkaline media, coordination on the secondary alcohol group is followed by
liberation of a proton. With these conditions, chelate rings can be formed and complexes of significantly greater stability are formed.

Few data have been found for tin gluconate complexes in the available literature. Marksin et al. [46] reported that tin forms Sn(GH₄)⁺ and Sn(GH₄)₂, with the former predominating at elevated temperatures and with excess gluconate ions. A voltammetric study by Vasantha et al. [47] revealed that under transient condition in neutral pH gluconate solutions, the electroactive species are Sn(GH₄)⁺, whose formation is slow.
Gluconate complex species of cobalt [48] have been found to be Co(GH₄)⁺ in solutions of pH < 7.5. Pink, gel-type precipitates, with the structure of Co₂(OH)₃(GH₄)·xH₂O and Co₃(GH₄)₂(OH)₂ 2H₂O, form in solutions of pH 7.5–9.5. Above pH 9.5, an anionic species, which is subject to rapid auto-oxidation, exists in solution.

Table 3.2 gives the stability constant values of the gluconate complex species which can exist in the sulfate/gluconate bath. It can be seen that the Co(GH₄)⁺ species has the lowest stability. As might be expected for such an unstable species, ionic strength has a significant effect on its stability [48]. The value of logK is 0.38, 0.46, and 0.68 for ionic strengths of 0.4, 0.2, and 0.1M respectively.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Log K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HGH₄</td>
<td>3.70</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>3.01</td>
<td></td>
</tr>
<tr>
<td>Sn(GH₄)⁺</td>
<td>2.86</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>2.78</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>2.28</td>
<td>20</td>
</tr>
<tr>
<td>Sn(GH₄)₂</td>
<td>1.58</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>35</td>
</tr>
<tr>
<td>Co(GH₄)⁺</td>
<td>0.57</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2.3 Electrochemical behaviour of the bath

The overall and partial potentiodynamic cathodic polarisation curves of the tin-cobalt alloy deposition from a sulfate/gluconate bath were traced by Rehim et al. [44]. They show that the individual discharge of both tin and cobalt is accompanied by large polarisations. The deposition potential for tin shifts from −800 mV to −1600 mV, which depends on the tin ion concentration in the solution. However, the cobalt is deposited at about −1200 mV and this deposition potential is hardly affected by the change in cobalt ion concentration. The position of polarisation curves of tin-cobalt alloys with respect to those of the parent metals
depends greatly on the concentration of tin ions in the bulk electrolyte. At high tin ion concentrations, tin is more noble than cobalt and the overall polarisation curves lie to the less negative potential side of the individual curves of cobalt. At low tin ion concentrations, tin is less noble than cobalt and the overall polarisation curves lie to the more negative potential side of the individual curves of cobalt. In all cases, the polarisation curves of the alloy are found to lie between those of the parent metals of tin and cobalt. This implies that the codeposition enables the less noble metal to deposit at more positive potentials and the more noble metal to deposit at more negative potentials.

3.3 Fluoride bath

Compared with the dilute sulfate electrolyte, the metal concentrations are much higher in the fluoride bath (Table 3.3). The most interesting feature of fluoride bath is its ability to deposit tin-cobalt alloy coatings of substantially constant composition over a wide range of bath variables, such as pH, current density, and concentration of the metal salts. According to Miyashita et al. [51], increasing cobalt chloride concentration in the bath from 400 to 600 g/l, actually made no difference to the cobalt content in the deposit; further increasing to 1000 g/l increased the cobalt percent in the deposit only from 21.6 to 26.1. The effects of tin in the electrolyte, and other operating parameters were completely negligible.

No information can be found in the literature on the codeposition mechanisms of tin and cobalt from the fluoride bath. However, the explanation on the codeposition behaviour of tin and nickel from a similar fluoride bath may be cited, since the same insensitivity of deposit composition to the solution formulation and the operation parameters has also been observed during the electrodeposition of tin-nickel alloys [50]. It has been suggested that the composition constancy of tin-nickel alloy electrodeposits may be either due to the direct discharge of NiSn from a polynuclear complex ion, containing both metals in the same proportions, or due to the fortuitous matching of the two metal deposition rates over a wide current density range.
Table 3.3 Fluoride baths in the literature

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin salt g/l</td>
<td>50 (SnF&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>50 (SnCl&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O)</td>
<td>26 (SnCl&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O)</td>
</tr>
<tr>
<td>Cobalt chloride g/l</td>
<td>500</td>
<td>250</td>
<td>125</td>
</tr>
<tr>
<td>Complexing agent g/l</td>
<td>20 (NaF·HF)</td>
<td>100 (NH&lt;sub&gt;4&lt;/sub&gt;HF&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>(NH&lt;sub&gt;4&lt;/sub&gt;HF&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Addition agents</td>
<td>35 ml/l NH&lt;sub&gt;3&lt;/sub&gt; soln. (sg 0.88)</td>
<td>100 ml/l HCl (10N)</td>
<td>thiourea</td>
</tr>
<tr>
<td>pH</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature °C</td>
<td>65~80</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>Current density A/dm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.5~4</td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td>Deposit composition (Cobalt in deposit wt.%)</td>
<td>20~25</td>
<td>33.3</td>
<td>20~25</td>
</tr>
</tbody>
</table>

3.4 Pyrophosphate bath

The colour similarity of tin-cobalt alloy deposits to that of chromium coatings underlies the development of various electroplating processes. Tin-cobalt alloy electroplating from the pyrophosphate bath was published as early as 1960 by Sree and Rama Char [35]. However, this kind of bath produced relatively less interest than the sulfate/gluconate bath and fluoride bath because the colour of its deposits varied only from white to dark grey in the composition range 0-87% cobalt.
According to Sree and Rama Char [35], the bath consisted of stannous pyrophosphate, cobalt chloride and a large excess of potassium pyrophosphate (molar ratio of pyrophosphate to metal 2.5). It was operated with a platinum anode at a pH of 9.5–10 and at a temperature of 40–80°C, meanwhile an agitation of 800 revolution/minute was applied. The cobalt content in the alloy increased with increase in the cobalt content of the solution and current density, and decrease in temperature or agitation. The increasing trend levelled off when the cobalt content in the alloy approached the metal content of cobalt in the solution. Variation in the pH and pyrophosphate content had little effect. To obtain deposits of better surface quality, some addition agents were tried, including ammonium citrate, gelatine, dextrin, boric acid, ammonium bifluoride, hydroquinone plus sodium sulphite. As a result, a bright deposit of high cobalt content was obtained, but the cathode current efficiency was claimed to be rather low (49% for Sn-45Co alloys obtained at 9.8A/dm²).

### 3.5 Deposit structure and properties

The phase diagram (Figure 3.1) for cast tin-cobalt alloys shows that there exist three intermetallic phases of different structures [54]:

- $\text{CoSn}_2$ (19.8 wt.% Co), tetragonal, unit cell size: $a=6.348$ Å, $c=5.441$ Å
- $\text{CoSn}$ (33.3 wt.% Co), hexagonal, unit cell size: $a=5.268$ Å, $c=4.249$ Å
- $\gamma\text{Co}_3\text{Sn}_2$ (40.7 to 41.7 wt.% Co), possibly hexagonal, unit cell size: $a=16.356$ Å, $c=5.198$ Å

However, the structural analysis of the as-plated tin-cobalt alloys by different authors came to quite different conclusions.

On the basis of this phase diagram, Hemsley and Roper [37] claimed that the electrodeposited tin-20% cobalt alloy from the mildly alkaline sulfate/gluconate bath was likely to be the tetragonal form of $\text{CoSn}_2$. On the other hand, the X-ray diffraction studies of Clark et al. [52] showed that the tin-33.3% cobalt alloy obtained from their acid fluoride bath crystallized with a cubic structure differing from the hexagonal cast $\text{CoSn}$. The cubic $\text{CoSn}$ in the as-plated deposits was metastable and underwent decomposition into $\text{CoSn}_2$ and $\gamma\text{Co}_3\text{Sn}_2$ when heat treated at a temperature of above 200°C.
CHAPTER 3 TIN-COBALT ALLOYS

Using Mössbauer and X-ray measurements and the cast tin-cobalt alloy \( \gamma \text{Co}_3\text{Sn}_2 \) (hexagonal) and CoSn (tetragonal) as the reference, Jaen et al. [55] identified that the components of the electrodeposited tin-cobalt alloys obtained from a mildly alkaline sulfate/gluconate bath, similar to the one described by Hemsley and Roper [37], were \( \gamma \text{Co}_3\text{Sn}_2 \) (hexagonal), CoSn (cubic) and dissolved metallic tin when the cobalt content in deposits was 35% and 40%. In the deposits of 20-25% and 30% cobalt, only CoSn and dissolved tin but no \( \gamma \text{Co}_3\text{Sn}_2 \) were detected. The presence of cubic CoSn, which does not appear in the phase diagram, in all the studied samples and the fact that it is the phase likely to be formed from different types of electroplating solutions (acid fluoride or mild alkaline baths) makes the author suggest that the cubic CoSn phase is always one of the main components of the electrodeposited tin-cobalt alloy. Contrary to Hemsley and Roper's conclusion, no indication of the presence of CoSn\(_2\) phase was found.

More recent research by Sujatha et al. [43] showed the distinct changes in the alloy phase components with increase in cobalt content of the deposits from a neutral gluconate bath. With 5% cobalt, the alloy exists almost as tin, with 10% cobalt, as a mixture of Sn and CoSn phase, with 20% alloy as a mixture of CoSn and CoSn\(_2\), with 29-35% mainly as CoSn phase and above 50%, as a mixture of \( \gamma \text{Co}_3\text{Sn}_2 \) in CoSn. The alloy deposits showed a heterogeneous phase structure for the alloy containing 25-29% cobalt, a single phase fine grained structure for the tin-35% cobalt alloy, and a cracked structure for an alloy containing more than 50% cobalt.

The hardness of the tin-20% cobalt alloy was reported to range from 390 to 410 VPN and, as would be expected, hardness has been found to increase with increasing cobalt content in the deposit [37, 56]. Miyashita and Kurihara [51] reported that the hardness of the deposits from fluoride baths increases from 359 HV at 15.9% cobalt to 550 HV at 26.1% cobalt. However, the microhardness measured at a load of 10 g by Sujatha et al. [43] was appreciably lower than the previous results. The hardness showed a gradual increase from 28 VHN at 5% Cobalt to 73 VHN at 20% cobalt. There appeared a sudden increase of the hardness to 187 VHN when the cobalt content exceeds about 30%. Almost no difference in hardness (224-225VHN) was observed between the deposits containing 35% and 45% cobalt.
Corrosion tests showed that under many circumstances tin-cobalt alloy is able to yield corrosion protection which is similar to that obtained with chromium [37]. The good corrosion resistance of tin-cobalt alloy is believed due to the presence of an air-formed film on the surface. The nature of the film on the tin-33% cobalt alloy deposits from fluoride bath was found to exist in several stage of oxidation [52, 57], while Thomas and Sharma [58] reported that the film mainly consisted of hydrated tin(IV) oxide.

3.6 Electrolyte stability

With tin compounds, the tetravalent state is more stable than the divalent state, although only slightly. In aqueous solutions, tin(II) ions are readily oxidised to tin(IV) by atmospheric oxygen. This leads to a universal problem of electrolyte stability in the electroplating of tin and its alloys. The loss of tin(II) ions from the electrolyte has a two-fold effect. On the one hand, the oxidation of tin(II) ions forms either soluble or insoluble tin(IV) products, which do not take any part in the electrodeposition process. On the other hand, absorption of tin(II) ions on the insoluble tin(IV) products, which usually exist as the sludge in the bath, promotes the loss of active species.

The extent to which stannous ion are lost from the solution as a function of time is dependent on the anion type, tin(II) ion concentration, temperature, agitation strength, various impurities and the addition of antioxidants. With regard to the anion types, it was found that tin(II) ions are only slowly oxidised in perchloric acid solutions [59]; but that the oxidation is considerably more rapid in solutions of sulfuric or hydrochloric acids. McCarthy [60] reported that oxidation of tin (II) to (IV) took place most rapidly in fluoroborate and sulfamate baths. Research results by Meibuhr et al. [61] revealed that tin(II) was lost rapidly from the halide solutions in the order Br\textsuperscript{−} > Cl\textsuperscript{−} > F\textsuperscript{−}.

Electroplating conditions such as agitation and temperature also play a role in the oxidation of stannous ions [62]. In high speed electroplating process, for example, the rapid pump action and solution movement common to high speed electroplating machines cause air to be mixed with the solution, thereby promoting such oxidation. This oxidation is, on the other hand, accelerated due to the elevated temperature of operation which is commonly
used in high speed electroplating installations. On this basis, air agitation technology is usually not used in tin(II) solution.

Fortunately, oxidation of stannous ions in the solution can be inhibited or at least suppressed by the addition of some appropriate organic compounds such as sulphonic acids [50, 61, 63], and hydroxyphenyl compounds [62]. The use of phenol- or cresol-sulphonic acids for stabilising tin sulfate baths is a practise of very long standing. Phenolsulphonic acid (PSA) is found to be the most effective stabiliser compared with other compounds. The preferred hydroxyphenyl compounds includes pyrocatechol, hydroquinone, resorcinol, phloroglucinol, pyrogallol, 3-amino phenol, or hydroquinone sulphonic acid ester.

The mechanism of oxidation inhibition is not completely clear. It is assumed that the oxidation inhibitor might form a complex with stannous ions, or tie up the soluble oxygen in solution, or reduce the oxygen solubility, or be preferentially oxidised by the oxygen. However, polarographic investigations [64-65] of the tin(II) stability in the presence of some antioxidants shows that enhanced stability is due to neither complexation of tin(II) nor reduction of oxygen. The fact that some inhibitors, such as pyrogallo, are effective in very small concentrations [64], and are not used up at a rapid rate suggests that these inhibitors are not behaving as a reducing agent for dissolved oxygen. The possible explanation of the inhibition is suggested to be that the reaction between tin(II) and oxygen is a chain reaction which is inhibited by the inhibitor.
4 Pulsed current electroplating

4.1 Introduction

Electrodeposition of metal and alloys is normally carried out with a direct current (DC) power supply. The delivered current during such electroplating is kept at a constant magnitude, although there is inevitably some degree of current ripple. It is the applied current density that controls the properties of the deposits from a specific electrolyte.

In contrast, pulsed current electroplating uses a periodic variation of current. The amplitude or even the direction of the applied current changes as a function of time. The advantage of using pulsed current over conventional, direct current, has been established as the improvement of properties of deposits, such as more uniform thickness distribution, finer grain sized structure, higher purity and greater ductility. Pulsed current electroplating also makes possible the electrodeposition of some alloy compositions which cannot be obtained under direct current conditions [66, 67]. In addition, pulsed current electroplating offers more physical parameters to modify the deposit quality than DC electroplating, where only the applied current density could be employed.

Although the theoretical and practical aspects of pulse electroplating [68] have been studied extensively and the beneficial effects of using pulsed current have been recognised for a long time, pulsed current electroplating is not as widely applied as DC electroplating. The most common application for pulsed current electroplating is the precious metal electroplating in the decorative industry and the electronics industry, and copper electroplating for through holes in printed circuit boards (PCBs). The major reason for the relatively slow expansion is that pulsed current electroplating requires a special current rectifier with high voltage and quick response, which is much more expensive than conventional rectifiers. Therefore, any potential application of pulse electroplating should justify the capital equipment cost.
4.2 Waveform overview

The applied current in pulsed current electroplating varies periodically with time and thus forms a certain kind of waveform. Theoretically any current waveform could be used in pulsed current electroplating. Meanwhile, advances in modern electronics allow the current to be applied as almost any function of time. However, in practice there are mainly two waveforms of interest for the laboratory and industrial pulsed current electroplating. They are the sinusoidal wave and the square wave.

4.2.1 Sinusoidal Wave

In the early days of pulse electroplating, because of less developed electronics, modified sinusoidal waves were commonly used. The most frequently applied sinusoidal waveforms include the superimposed sine-wave, the half wave phased delayed, the full-wave phase delayed, and the skip-sine wave [69]. Figure 4.1 shows some typical sinusoidal waveforms.

Investigations involving sinusoidal waves concentrated on the investigation of the effect of superimposed alternating current on the electrodeposition of single metals [70-71] and alloys [72-73]. The general conclusion reached was that the effect of alternating current diminishes with increasing either the magnitude of the direct current or the frequency of the alternating current. At high frequencies, the contribution from the alternating current becomes negligible.

The modified sine-wave system usually uses the power line frequency of 50 to 60 Hz half wave or 100 to 120 Hz full wave as its time base. The output pulse has a fast pulse rise time and a slow turn-off time following the slow decay of the sine-wave [69]. The advantage of the modified sine-wave is low cost by comparison with square-wave. However, a sinusoidal wave does not offer as much benefit as a square one, so it has not found industrial acceptance for pulse electrodeposition.
4.2.2 Square Wave

Square current waveforms in all frequency regimes and combinations of these are in general use nowadays. Figure 4.2 illustrates several typical shapes of square waves. Depending on whether the current direction changes or not during the whole cycle, square waveforms are divided into two categories, i.e. the unipolar and the bipolar pulse waves. For a unipolar pulse wave, the current is unidirectional and always cathodic. (Fig. 4.2 (a) and (b)). On the contrary, the current of a bipolar pulse wave changes its direction alternately from being cathodic to being anodic (Figure 4.2 (c), (d), (e)). Obviously, bipolar pulse waves normally have more complex shapes than unipolar ones. According to the convention in the literature, the following abbreviations of applied waveforms are frequently used:

- **PC** Pulsed Current (or on/off electroplating, pulse-pause electroplating), referring to a unipolar wave with a cathodic pulse followed by a period of zero current (Figure 4.2 (a))
- **PR** Pulsed Reverse or Periodic Reversal, meaning a bipolar wave with a cathodic pulse followed by an anodic pulse, with or without an interval of zero current in between (Figure 4.2 (c) or (d)). In general, PR wave without an off-time is preferred.
- **PPR** Pulsed Pulse Reverse, referring to a wave with a pulsed cathodic pulse following by a pulsed anodic pulse (Figure 4.2 (e)).

During PC electroplating, a much higher instantaneous current density than that for DC electroplating is used (only for a short period of time). This results in a very negative cathode potential, which will greatly influence the nucleation rate because a high energy is available for the formation of new nuclei [74]. Moreover, during the period of zero current, some important phenomena such as adsorption-desorption as well as recrystallisation of the deposit could occur. Consequently PC wave has been broadly used to modify the crystallisation process of the electrodeposited metal by increasing the nucleation rate and hence refining the grain size, and by decreasing the inclusion of foreign materials including hydrogen. As a result, deposits become denser and purer, and show improved properties.
CHAPTER 4 PULSED CURRENT PLATING

For a PR wave, the main purpose of inverting the current from cathodic to anodic during a short fraction of the total period is to remove metal preferentially from areas that attract more current than others due to the non-uniform current distribution during the cathodic part of the cycle. Areas exposed to concentration of current density are preferentially plated in the cathodic cycle, but for the same reason, they are preferentially dissolved in the anodic cycle. Consequently the electroplating thickness distribution should be considerably improved. It is also possible to retard the development of dendrite formation with a PR wave. On the other hand, modifications in the deposit structure, mainly grain size, in PC electroplating can also be achieved with PR waves because of forced nucleation at each new cathodic pulse.

PPR wave features a pulsed current during both cathodic and anodic periods. With optimisation of electrical parameters, this approach could offer a combination of the advantages of PC electroplating with respect to modification of deposit structure and properties, with those of anodic dissolving in improving the thickness distribution. The use of pulsed current allows a substantial increase in current density in both anodic and cathodic cycles. During the cathodic period pulsed current leads to grain refinement normally associated with PC electroplating, and this is further favoured by the disturbance of growth sites by periodic inversion of the current. Thickness distribution of deposits obtained with PPR wave is also improved, not only by the normal anodic dissolution of metal from high spots or other exposed areas as in PR electroplating, but also because the preferential dissolution can be significantly enhanced by application of relatively short anodic pulses of high amplitude. Full advantage can be taken of this method only if all electrical parameters can be set independently, and in particular, if cathodic and anodic pulses can be independently regulated, e.g., with respect to pulse length and amplitude. Finally, it must be pointed out that PR or PPR electroplating is usually suitable for the situation where the deposit is ready to dissolve in the electrolyte, otherwise passivation can occur.

In summary, every type of square waveform has its own characteristics. The correct choice of current waveforms for pulsed current electroplating will depend on the equipment characteristics, electrolyte chemistry, the electroplating conditions, and ultimately the application.
4.3 Variables in pulsed current electroplating

Figure 4.3 demonstrates three independent variables to describe a wave quantitatively, which is of primary importance in pulsed current electroplating. These are (1) the peak current density \( j_p \), which could be cathodic or anodic in polarity; (2) the on-time \( t_{on} \), during which the current flows through the circuit; (3) the off-time \( t_{off} \), during which there is no current.

From these basic parameters, several other variables are derived to illuminate further the characteristics of a waveform. These include:

- Frequency \( f \)
- Duty cycle \( \theta \)
- Average (or mean) current density \( j_m \).

The frequency is defined as the number of cycles in one second. Thus,

\[
f = \frac{1}{\text{cycle time}} = \frac{1}{T} = \frac{1}{t_{on} + t_{off}} \quad \text{Hz} \quad (4.1)
\]

The frequency in most applications falls in the range of less than 200 Hz in order to avoid the damping of faradaic current caused by the capacitance of the electrical double layer [68, 74]. Conventional view believes that the electrode response at high frequency will approach that of a DC current and hence the benefits of pulse electroplating are nullified. However, a recent study by Tantavichet and Pritzker [75] suggests that even at a frequency of 50 kHz, the electrode potential during pulsed current electrodeposition of copper onto a RDE does not completely converge to that of DC electrolysis. Nevertheless, the application of low frequency is important, if the process is to be used on an industrial scale.

The duty cycle is the ratio of the on-time to the sum of on-time and off-time:

\[
\theta = \frac{t_{on}}{t_{on} + t_{off}} \times 100\% \quad (4.2)
\]
As duty cycle is increased the pulsed current begins to approach a direct current. A wave with a duty cycle of 100 percent corresponds to a DC signal because there is no off-time.

The average current density is the arithmetic average of the applied current during a cycle. The average current density decides the overall deposition rate, whereas the peak current density is responsible for the instantaneous deposition rate. The average current density of a PC current wave can be calculated by:

\[ j_m = \frac{j_p t_{on}}{t_{on} + t_{off}} = j_p \theta \]  \hspace{1cm} (4.3)

From this equation, it shows that the instantaneous peak current density \( j_p \) can be many times higher than the average current density \( j_m \), depending on the value of duty cycle \( \theta \). For example, when \( \theta \) is 1\%, \( j_p = 100 \) \( i_m \); when \( \theta \) is 0.1\%, \( j_p = 1000 \) \( j_m \). From a practical viewpoint, this feature imposes a limitation on the usable duty cycle of a pulsed current waveform due to the limitation of the rectifier capacity. If sufficient spare rectifier capacity is available a duty cycle of 33 to 50\% is probably the minimum practical value. For applications using high current density, such as chromium electroplating, a value of 50 to 75\% would be the lowest usable duty cycle.

Pulsed current electroplating offers more control variables over traditional DC electroplating. This gives a high degree of flexibility on choosing deposition conditions. Unfortunately this flexibility or freedom leads to complexity as well. A large number of experiments have to be carried out to find the optimised deposition parameters. This high degree of complexity decreases the chance of successful utilisation of the technology. Statistical designs of experiments was suggested by some researchers [76, 77] to reduce the number of experiments.

4.4 Mass transport characteristics

4.4.1 Model of a duplex diffusion layer

According to the Nernst diffusion layer theory [78], there exist two regions near the surface of the electrode during DC electroplating, i.e. the diffusion region and the convective region as shown in Figure 4.4. The diffusion region is a very thin stationary
layer in contact with the electrode. Within this layer, diffusion alone controls the mass transfer of the electroactive species to the electrode. The concentration gradient of the electroactive species throughout the diffusion layer, is linear and decided by the applied current density as:

$$\frac{dc}{dx} = \frac{C_s - C_x}{\delta_N} = \frac{j}{nFD_o}$$  \hspace{1cm} (4.4)

where \( j \) is the applied current density, \( D_o \) is the diffusion coefficient of the depositing species, \( n \) the number of electrons involved in the deposition reaction, and \( F \) the Faraday constant. Outside the diffusion layer is the convective region, where mass transport by convection predominates and the concentration of the considered species is maintained at its value in the bulk solution.

One important aspect in pulsed current electroplating is a modification of the diffusion layer. Ibl [74] extended the linear Nernst diffusion layer model to the case of pulse electroplating and developed an approximate duplex diffusion layer model, which helps to understand the phenomena involved.

As Ibl suggested, there are two diffusion layers close to the electrode under pulsed current electroplating conditions (Figure 4.5). In the immediate vicinity of the electrode there exists a non-stationary diffusion layer. The concentration in this diffusion layer pulsates with the variation of the current: it decreases when the current is on and relaxes when the current is off. The thickness of the pulsating diffusion layer (\( \delta_p \)) is given by Equation 4.5

$$\delta_p = \sqrt{2D_o \tau_{on}(1-\theta)}$$  \hspace{1cm} (4.5)

Further out from the non-stationary pulsating diffusion layer is a stationary diffusion layer. The concentration of electroactive species in this layer does not vary with time after the stationary state is reached. Through this outer stationary diffusion layer, electroactive species are transported from the bulk of the solution towards the pulsating diffusion layer by diffusion at a rate corresponding to the average current density. It is this supply which allows the relaxation of the pulsating diffusion layer during the off-time. The extent of this diffusion layer is the same as that of DC electrolysis under the same hydrodynamic conditions. We thus have:

$$\delta_p + \delta_s = \delta_N$$  \hspace{1cm} (4.6)
where $\delta_N$ is the total diffusion layer thickness controlled by the hydrodynamic conditions, $\delta_s$ is the thickness of the stationary diffusion layer.

### 4.4.2 Surface concentration

As described by the duplex diffusion layer model, the concentration of the electroactive species at the electrode surface will oscillate between two extreme values, one at the end of each on-time or off-time, after a stationary state is reached. With some simplifying assumptions, these concentration changes at the electrode under pulsed current condition can be quantified by mathematical treatment.

The simplifying assumptions include [79, 80]:

- Planar cathode and well-defined hydrodynamic conditions;
- Non-faradaic component of the applied current and the electrical migration of the electroactive species are considered negligible due to the relatively high conductivity of most electroplating solutions;
- Diffusion is the only method of mass transport to the electrode surface;
- The diffusion coefficient is independent of the concentration of the species considered;
- No depletion of the species considered in the bulk solution

Under these conditions, the concentration of the species considered is governed by Fick’s second law of diffusion and three boundary conditions. The differential diffusion equation subject to different boundary conditions corresponding to different pulsed current waveform, was originally solved by Roseburgh and Miller [79]. The two extreme values of the surface concentration, i.e. $C_{s1}$ and $C_{s2}$ (Figure 4.5), were given as:

At the end of the off-time,

$$\frac{(C_o - C_{s1}) nFD_o}{j_o \delta_N} = \frac{8}{\pi^2} \sum \frac{1}{m^2} \frac{e^{m^2 \alpha T} - e^{m^2 \alpha_{of}}}{e^{m^2 \alpha T} - 1} \tag{4.7}$$

At the end of the on-time,

$$\frac{(C_o - C_{s2}) nFD_o}{j_o \delta_N} = 1 - \frac{8}{\pi^2} \sum \frac{1}{m^2} \frac{e^{m^2 \alpha T} - e^{m^2 \alpha_{of}}}{e^{m^2 \alpha T} - 1} \tag{4.8}$$
where $C_{i1}$, $C_{i2}$ are the surface concentration of the electrodeposited ions at the end of the off-time and on-time, respectively. $C_o$ is the concentration of the ions in the bulk solution.

$$m = 2n-1, n = 1, 2, 3, \ldots \infty. \alpha = \frac{\pi^2 D}{4\delta_n^2}. T \text{ is the cycle time and } T = t_{\text{on}} + t_{\text{off}}$$

From equations (4.7) and (4.8), the centre of the concentration oscillation or the average value of the concentration change at the electrode surface can be calculated by halving the sum of the extreme values of the surface concentration changes. The amplitude or the greatest deviation of the concentration above and below its average value may be obtained by taking half the difference of the values given by equations (4.7) and (4.8). Therefore, the expression for the average value of the surface concentration pulsation $C_m$ is:

$$C_m = nFD_0 \left( \frac{C_o - C_m}{i_p \delta_N} \right) \left( \frac{1}{2} + \frac{4}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \frac{e^{m^2 \alpha \text{on}} - e^{m^2 \alpha \text{off}}}{e^{m^2 \alpha T} - 1} \right)$$ (4.9)

the expression of the amplitude of the surface concentration pulsation is

$$\frac{C_{i1} - C_{i2}}{2} = \frac{i_p \delta_N}{nFD_0} \left( \frac{1}{2} + \frac{4}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \frac{e^{m^2 \alpha \text{on}} + e^{m^2 \alpha \text{off}} - 2e^{m^2 \alpha T}}{e^{m^2 \alpha T} - 1} \right)$$ (4.10)

Obviously, for very large on-times and off-times, which last long enough to bring about a linear distribution of concentration throughout the diffusion layer, the surface concentration oscillates between $C_o$ and $C_o - \frac{i_p \delta_N}{nFD_0}$, with the oscillation centre situate at

$$C_m = C_o - \frac{1}{2 \frac{i_p \delta_N}{nFD_0}}$$ (4.11)

On the other hand, if $\alpha T$ is very small, which corresponds to very short on-times and off-times, and a thick diffusion layer, the oscillation centre of the surface concentration is

$$C_m = C_o - \frac{i_p \delta_N}{nFD_0} = C_o - \frac{i_m \delta_N}{nFD_0}$$ (4.12)

and the amplitude is very small. In this case, the surface concentration is practically the same as that of a direct current electroplating at the same average current density [79].
When mass transport, under pulsed current conditions, to the electrode surface by convection is not negligible, the concentration of the reacting species should be described by the convective diffusion equation, which makes the mathematical treatment extremely difficult. Only rigorous numerical solutions [81-83] are available for the calculation of the surface concentration under such conditions. However, as reported by Viswanathan et al. [81], for short pulses under reasonable convective conditions, calculations based on simplified diffusion model yields adequate results.

4.4.3 Limitations from mass transport

There exist two kinds of limitations of the useful range of pulse conditions due to mass transport effects [68, 74, 80]. These two limitations arise from the depletion of cations in the non-stationary diffusion layer and the outer stationary diffusion layer, respectively. The depletion of the cations in the non-stationary diffusion layer limits the peak current density, whereas the depletion in the outer stationary diffusion layer limits the average current density [68].

For an applied peak current density higher than the direct current limiting value, if the on-time is long enough, the surface concentration of the reacting species will decrease with time to zero before the end of the on-time. Therefore a depletion of cations in the non-stationary diffusion layer occurs. The maximum pulse duration for an applied current density, at the end of which the surface concentration comes to zero, is called the transition time $\tau$ [74, 84]. It manifests itself experimentally by a sudden increase of the electrode potential which initiates an additional cathodic discharge reaction such as hydrogen evolution [85]. Or on the other hand, for a constant on-time and off-time, the surface concentration of the reacting species at the end of on-time will decrease with increase in the applied peak current density and reaches zero at a certain peak current density value. This peak current density is defined as the pulse limiting current density by Cheh [80]. In nature, the pulse limiting current density is the maximum peak current density that could be applied with a current efficiency of 100 percent. To sum up, the first limitation in pulsed current electroplating due to mass transport is that the on-time should not exceed the transition time for a specific pulse waveform, or for a fixed on and off-time, the peak
current density should not exceed the pulse limiting value, as far as the current efficiency is concerned.

Obviously, the depletion of cations in the non-stationary diffusion layer does not necessarily mean a depletion in the outer stationary diffusion layer [74]. Depletion of cationic concentration in the outer stationary diffusion layer takes place when the corresponding average current density approaches the limiting current density under direct current conditions. In other words, the depletion of cationic concentration in the outer stationary diffusion layer limits the maximum average current density achievable by pulsed current.

Using Roseburgh and Miller's solution of the surface concentration at the electrode during the pulsed current electroplating, Cheh [80] calculated the pulse limiting current density as a function of the dimensionless on-time \( \frac{D \tau}{\delta^2} \) for different duty cycles, and pointed out that the value of the pulse limiting current density may far exceed that of the direct limiting current density depending on the pulsed current waveform. The lower the duty cycle and the shorter the on-time, the higher the pulse limiting current density. However the maximum average current density could not exceed the direct limiting value. This was verified by his results with gold pulse electroplating and later confirmed by Chin's [82] numerical solution of the diffusion equation.

In terms of a constant deposit quality, the practical current density can sometimes be increased in pulsed current electroplating as compared to direct current conditions [68]. However, this practical current density is still below the diffusion limiting current density and the increase is only modest and does not represent the main advantage of the pulsed current electroplating technique, which is to improve the properties of the deposits through structural modification due to a high instantaneous peak current density [80].

4.5 Capacitance effect

At the interface between the electrode and the solution, there exists an electrical double layer the structure of which was described by different models [86]. In nature, the electrical
double layer behaves like a parallel plate capacitor. Its corresponding capacitance \((C_{dl})\) is very high, typically around 40-50 \(\mu\) F \(\text{cm}^{-2}\), due to the fact that the thickness of the electrical double layer is normally a few Ångstroms \([68]\). In electrodeposition, the electrical double layer must be charged up in order to provide an overpotential necessary for metal deposition to take place. In visualisation of the reaction at the electrode/solution interface during electrodeposition, an equivalent circuit of a capacitor \(C_{dl}\) and a resistor \(R_{ct}\) connected in parallel is usually considered, in which the capacitor \(C_{dl}\) represents the electrical double layer, and the resistor \(R_{ct}\) models the charge transfer resistance for metal deposition. The current used to charge up the electrical double layer is the so-called non-faradaic or capacitive current \(j_c\), while the current flowing through the resistor is used to deposit metal and is defined as faradaic current \(j_F\). The total current is the sum of the faradaic and capacitive components.

Like a normal capacitor, charging or discharging of the electrical double layer takes a period of time, which is dependent on both the applied current density and the physiochemical characteristics of the whole system. In pulsed current electroplating, both the charging and discharging time bring about some restrictions on the choice of waveform parameters. Generally, the on-time and off-time must be long enough so as to make the charging and discharging time negligible. Otherwise, damping of the faradaic current \([68]\) will happen. In the extreme cases, where the charging and discharging time of the double layer are much longer than the on-time and off-time, the faradaic current only oscillates around an average value and becomes virtually a direct current. As a consequence of the strong capacitive effect, the potential benefits of pulsed current are lost. This limits the maximum useful frequency to around 500 Hz for most applications; however, higher frequencies can be used where very high peak current densities are employed because the double layer charging and discharging times become shorter as a peak current density is increased.

Calculation of charging and discharging time of the electrical double layer was presented by Puippe and IbI \([87]\). As they reported, the values of the double layer capacitance \(C_{dl}\), the exchange current density and some other electrochemical parameters for the charge transfer reaction are needed to accomplish the precise computation. These values, however, are not always available. On assuming a typical value of 40-50 \(\mu\) F \(\text{cm}^{-2}\) as the double layer...
capacitance and neglecting the effect of the exchange current density, the charging time \( t_c \) and the discharging time \( t_d \) were suggested to be estimated as follows:

\[
\begin{align*}
t_c &= \frac{17}{j_p} \\
t_d &= \frac{120}{j_p}
\end{align*}
\]  

(4.13) (4.14)

where \( t_c \) and \( t_d \) are in microseconds and \( j_p \) in A/cm\(^2\). These two equations allow the estimation of \( t_c \) and \( t_d \) in the absence of any other knowledge concerning the system involved. This estimation also provides a rapid method for the selection of reasonable values of \( t_{on} \) and \( t_{off} \) in relation to the applied peak current density \( i_p \) avoiding serious disturbances of the pulsed current by capacitance effects at the electrode/solution interface.

Moreover, the capacitive current required at the beginning of a pulse for charging the electrical double layer is not lost for the metal deposition. The charge is recovered during the off-time when the double layer is discharging [68]. This also explains the fact that damping of the faradaic current does not decrease the current efficiency for metal deposition [87].

### 4.6 Modifications of electrocrystallisation

Electrocrystallisation is a very important step of metal electrodeposition since it influences directly the structure of the deposits and structure-related properties. For the same reason, modification of the electrocrystallisation process offers an opportunity to control and improve deposit properties. It is in this field that pulsed current electrodeposition finds most of its applications.

The basic mechanism of electrocrystallisation was attributed to Bockris et al. [88-90]. According to Bockris et al., electrocrystallisation consists of two stages. At the first stage, cations in the bulk solution are transferred towards the cathode by convection, migration, and diffusion; they then cross the electrical double layer, and thereafter the charge transfer reaction takes place, so adatoms are formed on the electrode surface. At the second stage following the mass transport and charge transfer, the adatoms move on the surface of the
electrode to energetically favourable sites such as lattice steps, kinks, or vacancies, and finally incorporate in the crystal lattice and crystallisation takes place.

Incorporation of adatoms into the crystal lattice occurs either by the building up of existing crystals or the formation and growth of fresh nuclei. These two modes are in competition with each other and are influenced by different factors. As a consequence of the competition, deposits will have fine or even nano-sized grains [83, 91, 92], if the nucleation rather than the growth of existing crystals is favoured. On the contrary, the deposit grains will become coarse if the growth of the existing crystals is preferred.

Generally, high negative overpotential, high adatom population, and low adatom surface diffusion enhance the creation of new nuclei, while high adatom surface mobility, low population of adatoms, and low overpotentials favours the growth of old crystals [68].

In pulsed current electrodeposition, the crystallisation process is modified by

- Enhanced mass transport which leads to high adatom population [93];
- High instantaneous peak current density, which results in high overpotential [68, 93-95]. The rate of two dimensional nucleation ($v$) is related to the total overpotential [68] as:

$$v = k_1 \exp\left(-\frac{k_2}{|\eta|}\right)$$  \hspace{1cm} (4.15)

where $k_1$ and $k_2$ are constants, and $\eta$ is the total overpotential. From this equation, the nucleation rate increases exponentially with increasing overpotential.

- Adsorption-desorption reactions during the off-time [68, 96-97]. Adsorbed species on the electrode surface, such as organic brighteners, stress reducers, and many other possible molecules in the solution, greatly affect the surface diffusion rate of the adatoms. Surface diffusion is a physical attribute of the adatoms. It cannot be controlled by the current waveform. However, it is affected by the presence of other adsorbed species on the electrode. The adsorption isotherm of these species is a function of the potential, and therefore by modulating the current, the nature of the adsorbed species can continuously fluctuate. Depending on the adsorption and desorption rate constants, for given pulse parameters, adsorption or desorption of a species will influence surface diffusion in a different way than in direct current
electroplating, thus leading to different crystallisation mechanism and therefore to different properties of the deposit.

- Recrystallisation during the off-time [93]. Small grains are thermodynamically less stable than large ones because of high surface energy. Therefore they tend to coalesce and recrystallise. For this to occur, the surface should remain active during the off-time. Again depending on different adsorbed species, the surface may be inhibited, in which case no recrystallisation will occur, and the fine grains obtained during the on-time of electrolysis are stabilised.

Finally, in pulse electroplating with very high pulse current densities, the concentration of adatoms at the interface is so high during the pulse that there is no time for ordering them into crystal lattice, resulting in similar effects as in rapid quenching. Under proper conditions an amorphous structure is likely to be produced.

### 4.7 Metal and current distribution

The uniformity of deposits is of great importance for the electroplating industry. First, metal consumption for the same thickness specification is less when the coating is uniformly distributed over the whole surface of the parts, than when local overplating occurs. The decreased requirement for metal results in cost saving, which is especially true for precious metal electroplating. Secondly, uniform distribution of metal allows for more flexibility and freedom of design. For example, in through-hole electroplating of printed circuit boards (PCBs), high aspect ratio (ratio of board thickness to hole diameter) printed circuit boards of 10 to 20:1 or even greater were claimed to be possible at sufficiently high current densities due to a uniform distribution of the deposited copper [98-99].

In spite of the great importance of metal distribution, it is very difficult to achieve a uniform one in practice. The non-uniformity distribution of metal arises from the non-uniform current distribution, which depends on many diverse factors. Of these factors, the most important are [100, 101]:

- Geometrical factors: shape and size of the plating tank and the shapes and sizes of the electrodes; the position of the electrodes relative to each other and to the wall of the electrolytic cell.
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- The electrical conductivity of the solution and of the electrodes
- Electrochemical factors: the kinetics of the electrode reaction, i.e., the type of polarisation (activation polarisation or concentration polarisation) and its characteristics (the slope of the polarisation curve).

Depending on the prevailing factors under the conditions considered, the consequent current distribution could be divided into the following three categories [101-104]:

- Primary distribution, in which only the resistance (IR) of the electrolyte is considered. The activation and concentration polarisation resistance is neglected.
- Secondary distribution, in which the IR of the electrolyte and the activation overpotential are considered, but the concentration overpotential is neglected.
- Tertiary distribution, in which concentration polarisation in not negligible anymore. Both the activation and the concentration polarisation are considered.

4.7.1 Primary current distribution

Without taking into consideration the effect of electrochemical polarisation, the primary current distribution is a function of cell geometry only [102]. The pattern of primary current distribution is common in physics, identical to that adopted in ideal circumstance by the lines of force in electrostatic and magnetic fields [103]. Theoretically, it can be deduced from the geometry alone. In practice, it is only possible to determine it accurately for simple configurations. With complex configurations, only estimates could be available by the known methods of numerical analysis using a computer.

Due to the unique characteristics of the primary current distribution independent of electrical and electrochemical factors, it is clear that the primary current distribution is the same in pulsed current and in direct current electroplating [102]. Except for several simple electrode configurations [104], the primary current distribution is usually not uniform. Its improvement could only be achieved by using proper cell geometry design or using other artificial means, such as a current screen of plastic or other non-conducting materials [101, 105], a current thief, bipolar anode and extra anode [106-107].
4.7.2 Secondary current distribution

Electrode polarisation has a marked effect on the current distribution when it is sufficiently larger than or of the same order as the resistance of the electrolyte. The activation polarisation, which is due to the slowness of the charge transfer step, counteracts the influence of an irregular geometry and the resistance of the solution, and tends to equalise the current distribution \[102\] over the electrode surface. The current distribution in which activation polarisation resistance dominates is the so-called secondary current distribution. It is usually described by a dimensionless Wagner number, \( W_a \) \[104\]:

\[
W_a = \frac{\kappa}{L} \left( \frac{d\eta}{dj} \right)
\]  (4.16)

where \( \kappa \) is the electrolyte conductivity (S cm\(^{-1}\) or \( \Omega^{-1} \) cm\(^{-1}\))

\( L \) is the characteristic length depending on the electrode geometry (cm)

\( \frac{d\eta}{dj} \) is the slope of the polarisation curve (V A\(^{-1}\) cm\(^2\) )

This number represents the ratio of the activation resistance to the ohmic resistance of the electrolyte. As a rule, the larger the Wagner number, the more uniform the current distribution is.

Obviously, unlike the primary current distribution, the secondary current distribution, as indicated by the Wagner number, can be altered and controlled by changing the electrolyte composition and the electroplating conditions. Uniform secondary current distribution will be favoured by increasing the electrolyte conductivity (e.g. introducing sufficient neutral salts) and maximising the slope of the polarisation curve (e.g. using additives).

The activation overpotential for metal deposition obeys Tafel's law:

\[
\eta = a + b \ln j
\]  (4.17)

therefore, the slope of the polarisation curve \( \frac{d\eta}{dj} \) is inversely proportional to the current density, and thus \( W_a \) decreases with increasing current density. The primary current distribution prevails at high electroplating current densities and the subsequent metal distribution becomes worse than the secondary current distribution.
In pulsed current electroplating with simple pulse and pause waveform (PC waveform), the applied peak current density is much higher than the average current density. It may thus be expected that at the same average current density, the current distribution under pulsed current conditions will deteriorate and tends to a primary distribution [74, 102]. As evidence, the deterioration of the current distribution with pulsed current was used to carry out selective electrodeposition of gold and tin-lead solder [108]. However, there exist some contradicting results in the literature. A mathematical model by Chin [82] claimed that at small DC current densities, the current distribution will be less uniform with pulsed current, while at high DC current density, pulsed current will have more uniform current distribution.

Nevertheless, significant improvements in electroplating thickness distribution can be obtained from PR [109-110] and PPR [111-114] current under optimised conditions. The real reason behind these improvements, however, is not due to the improvement of secondary current distribution. The common explanation is that the secondary current distributions for the cathodic and the anodic pulses are the same in nature, i.e. non-uniform, but have opposite directions. This means the high current density area during the cathodic pulses still have high current density during the anodic pulses. Consequently the overplated areas are removed faster during the anodic pulses. This levelling mechanism works so well that sometimes no additives are needed to produce deposits with uniform thickness [110], which not only reduces the production cost but also make the process control much easier.

4.7.3 Tertiary current distribution

In tertiary current distribution one takes into account concentration overpotential. The concentration overpotential is due to the depletion of reaction species at the electrode/solution interface. Its influence on the current distribution depends on the ratio of the characteristic length $L$ to the thickness $\delta$ of the diffusion layer [104].

For a surface profile with $L << \delta$, which is usually called a microprofile, the peaks are better accessible to diffusion than the recess. The depletion of reaction species and
therefore the concentration overpotential tends to be smaller at the peaks where the activation overpotential is higher. In such a case, the concentration overpotential counteracts the equalising action of the activation overpotential. Current distribution tends to be non-uniform. Small heterogeneities of the cathode surface, or asperities are thus amplified and the roughness increases as the deposits becomes thicker. The current distribution over a microprofile, microthrowing power, is relevant for surface finishing involving metal deposition into small recessed. It is also important because of its influence on the roughness and the appearance of the deposits.

For a macroprofile with $L \gg \delta$, the diffusion layer is thin and follows the profile everywhere. The diffusion is equally accessible to the peaks and the recesses. The interface concentration of reaction species is lower, and therefore the concentration overpotential is higher at peaks where the current density tends to be higher for geometrical reasons. The increase of the concentration overpotential at the peaks opposes the increases in local current density there. For this reason, the concentration overpotential at the macroprofile/solution interface acts in the same direction as the activation overpotential and tends to make the current distribution more uniform.

In pulsed current electroplating, the thickness $\delta_p$ of the pulsating diffusion layer is very small because the peak current is only applied for a very short period of time. Therefore, a profile which is a microprofile under direct current conditions could be converted into a macroprofile when pulsed current is used [102]. A smoother deposit is then expected. As a fact, experimental study of the deposition of copper, silver, and cadmium by IbI [102] indicates that pulsed current electroplating allows a good throwing power over geometric irregularities with a characteristic length down to $\delta_p$ if the metal deposition is controlled by the mass transport through the pulsating diffusion layer, i.e. $t_{on} \gg \tau$. ($\tau$ is the transition time).

### 4.7.4 Effect of Current efficiency

Metal distribution might not follow the current distribution if the current efficiency is not 100 percent. It might become more or less uniform than the current distribution, depending on the relationship between the current efficiency and the current density [101]. If the
current efficiency increases with the current density [115], more metal is deposited at the high current density areas. Therefore the non-uniformity of the current distribution is amplified. If the current efficiency decreases with the current density, metal deposited at the high current density areas is decreased and the metal distribution is more uniform than the current distribution. Generally speaking, the metal distribution can be better in pulsed current electroplating when compared with direct current [111], in situations where hydrogen is codeposited (current efficiency less than 100%).
5 Compositionally modulated multilayer (CMM) coatings

5.1 Introduction

A new class of materials, known as compositionally modulated multilayer (CMM) coatings, has generated considerable interest in recent years [116-120]. Such multilayered coatings are characteristic of a structure with periodically alternating thin layers (ranging from a few nanometres to a few microns) of two different metals or alloys. As a result of the layering at such a small scale, these coating materials can possess unique and outstanding physical and mechanical properties which are not obtainable in the parent materials. Property enhancement can be achieved in areas including supermodulus effect, improved magnetic, X-ray, optical, superconductive, and electrical properties, as well as improved strength and wear resistance, with such multilayered coatings [118].

Multilayer coating is not a new concept in surface engineering. In fact, it has been developed as a means of enhancing performance, especially the corrosion service life. Layering of electrodeposited coatings has been used with decorative chromium on steel substrate, where a three component system is utilised: an initial layer of copper promotes good adhesion to the substrate, an intermediate layer of nickel (5-30 μm) provides a barrier of high corrosion resistance and a final thin layer of chromium (0.2-2.0 μm) gives a hard, wear-resistant and decorative finish. Another analogous system is a gold finish (0.2-2.0 μm) and nickel underlayer (5-15 μm) on copper or brass [116]. However, these kind of multilayered coatings with few and relatively thick sublayers are not within the scope of interest of this research, which is mainly focused on multilayer coatings with composition modulations. The concept of "modulation" comes from the variation of deposit composition and structure in a more systematic and regular manner. Figure 5.1 shows a schematic representation of the cross-section of a CMM coating. Depending on the nature of the sublayers, the corresponding CMM coatings can form a metal/metal (e.g. Zn/Ni...
5.2 Electrodeposition technique of CMM coatings

Due to the layered structure, the prerequisites for a suitable deposition process for CMM coatings are as follows [128]:

- The process must produce well defined and regular thin layers and interfaces.
- Planar growth of the layers should predominate, which means the process has to be capable of producing a highly smooth surface.
- The layers produced have to be of a definite purity.
- The process may be required to produce multilayers at an atomic level.
- The interfaces between layers should be abrupt. Consequently, low temperature deposition process is preferred since with high process temperature inter-diffusion of the components could occur, particularly with very thin layers.
- The multilayered structure has to be reproducible.

In practice, there are three main techniques in competition with each other for the production of CMM coatings. These are physical vapour deposition (PVD) [129], chemical vapour deposition (CVD) [130] and electrodeposition. Although PVD (covering evaporation, sputtering and molecular beam epitaxy and ion plating) and CVD are often used for the production of CMM coatings, they suffer from some disadvantages (as shown in Table 5.1) such as high capital investment for PVD and high process temperature for CVD. The electrodeposition technique, on the contrary, offers a much less expensive method with certain advantages over the PVD and CVD technology, such as that there is the possibility of electroplating large scale surfaces in suitably sized process tanks and most electroplating solutions can be operated close to room temperature which minimises the risk of inter-diffusion between neighbouring layers during deposition (a potential problem with higher temperature process) so as to maintain the sharp interfaces produced. Although electrodeposition may also have some disadvantages such as poor throwing.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Vapour Deposition (PVD)</td>
<td>- Low deposition temperature</td>
<td>- Poor throwing power</td>
</tr>
<tr>
<td></td>
<td>- Ideal for components of close tolerances</td>
<td>- High vacuum ($10^{-2}$-$10^{-4}$ Torr) required</td>
</tr>
<tr>
<td></td>
<td>- Able to produce mirror finishes without post-coating polishing</td>
<td>- Expensive and sophisticated technology</td>
</tr>
<tr>
<td></td>
<td>- A large variety of substrate (metal, plastics and ceramics) can be coated</td>
<td>- Coating/substrate adhesion (physical bond) can be problematical</td>
</tr>
<tr>
<td></td>
<td>- No toxic pollutants or effluents are produced</td>
<td>- Not suitable for mass production</td>
</tr>
<tr>
<td>Chemical Vapour Deposition (CVD)</td>
<td>- Excellent throwing power</td>
<td>- High process temperature</td>
</tr>
<tr>
<td></td>
<td>- Very good coating/substrate adhesion (diffusion bond due to the reaction between the gaseous phases and the heated surface of the substrate)</td>
<td>- The high process temperature required limits the types of substrates which can be coated</td>
</tr>
<tr>
<td></td>
<td>- Able to deposit a very wide range of materials including ceramics</td>
<td>- Significant dimensional and geometrical change of the substrate</td>
</tr>
<tr>
<td></td>
<td>- Coatings of very high purity</td>
<td>- The chemical precursors are often hazardous and at times extremely toxic. The by-products of these precursors are also toxic and corrosive and must be neutralised.</td>
</tr>
<tr>
<td></td>
<td>- Suited for the mass production of small items</td>
<td>- Post-coating heat-treatment may be necessary</td>
</tr>
<tr>
<td>Electrodeposition</td>
<td>- Cheap and well-established industrial process</td>
<td>- Throwing power may be poor</td>
</tr>
<tr>
<td></td>
<td>- Room temperature operation and thus no risk of interdiffusion at interfaces</td>
<td>- Possible hydrogen embrittlement</td>
</tr>
<tr>
<td></td>
<td>- The possibility of electroplating large scale surfaces</td>
<td>- Difficulties encountered in producing ultra thin layers</td>
</tr>
<tr>
<td></td>
<td>- High deposition rate</td>
<td>- Not all metals can be electrodeposited and sometimes very difficult to deposit some metal couples</td>
</tr>
<tr>
<td></td>
<td>- Suitable for mass production</td>
<td></td>
</tr>
</tbody>
</table>
power and the difficulties in achieving very thin layered structures, with the use of proper 
electroplating processes and additives some of them could be overcome. Therefore the 
electrodeposition technique is generally competitive and, in many cases, preferred, for 
economic reasons.

Electrodeposition of CMM coatings has been carried out using two different approaches: 
electroplating either from two different electrolytes (dual bath technique) or from a single 
electrolyte (single bath technique), both having their advantages and disadvantages.

5.2.1 Dual bath technique (DBT)

The dual bath technique is probably the simpler of the two common electrodeposition 
techniques for CMM coatings. It involves the deposition, in an alternate fashion, of two 
component layers from two separate electrolytes. By definition, the dual bath technique 
requires the physical transfer of the substrates between baths and during each transfer the 
inter-bath rinse, which usually consists of rinsing in water and then in the next electrolyte 
to be used, in order to prevent the potential cross-contamination of the electrolytes.

The first ever reported attempt to produce CMM coatings by electrodeposition was carried 
out using the dual bath technique. In 1921, Blum [134] obtained Cu/Ni and Cu/Ag 
multilayer coatings by depositing alternate layers from two separate electrolytes and 
manually transferring the substrates in a repetitive mode. It was claimed that the 
compositionally modulated alloys obtained had a very small grain size and consequently a 
very high fracture strength. A similar technique was later employed to grow multilayer 
gratings of Au/Ag and Ag/Cu with repeat distances of 2.0 nm which only recently have 
been exceeded [117]. Haseeb et al. [135] have produced Cu/Ni compositionally modulated 
multilayers with a sublayer thickness down to less than 5 nm by the dual bath technique. A 
high-resolution electron microscopy study revealed that the multilayers, with distinct and 
continuous sublayers, grow in a columnar fashion. Within each columnar grain, the 
sublayers form epitaxially on top of each other. Other interest in the dual bath technique 
was centred around zinc alloy systems for corrosion resistance, these will be reviewed 
later.
Despite the long history and the simplicity of the dual bath technique in terms of solution chemistry and control, as well as the capability of this technique to produce alternate layers of a large variety of materials including pure metals and a wide range of alloys (even ternary and quaternary alloys), relatively limited work has been carried out on dual bath electrodeposition. The major drawback of the dual bath technique, which makes it unpopular, is the substrate transfer. First, the substrate transfer itself is laborious and time consuming, especially for the electrodeposition of CMM coatings with a sublayer thickness of a few nanometres (Note that for a 10 nm sublayer thickness there are 100 layers/μm, whilst the time necessary for the substrate transfer and rinsing depends on the number of layers deposited). Nabiram et al. [136] have demonstrated that in their automated, computer controlled multi-bath system for producing large-scale CMM coatings, the time needed for producing a 70 μm thick CMM coatings increases hyperbolically to 18 hours as the thickness of the sublayers is reduced to 25 nm. The time required for inter-bath transfer and rinsing would reduce the overall rate of deposition to unacceptable levels. This greatly hinders the scale-up of the process. Although Ross et al. [127] have made a successful attempt to build up an automated dual bath electrodeposition system (Figure 5.2) which eliminated the substrate transfer and was used to produce multilayers of nickel-phosphorus and other alloys with a repeat lengths of 19 Å and above, there were sample geometry restrictions: the plated coatings only covered a ring-shaped area. The second drawback with the DBT is that during substrate transfer and the inter-bath rinsing, the surface layer may be oxidised and formation of oxides may take place. This can adversely affect the properties of the deposits [119]. Finally, special attention may have to be paid to the deposition of a more noble component on a less noble one, as the dissolution of the less noble component and the displacement reaction by the more noble component may take place. Chawa et al. [122] observed that the current density required to electrodeposit nickel onto zinc needed to be maintained at high level during the initial stages of film formation to minimise zinc dissolution, which would otherwise lead to poor deposits.

5.2.2 Single bath technique (SBT)

The single bath technique involves only one electrolyte containing two different dissolved metals (A, B), from which a pure metal (A) and an alloy of the first metal A and the second, less noble metal B, are deposited successively by either changing the applied
current density [137, 138] or potential [139-141], by controlling diffusion near the cathode surface [142], by changing the agitation or by a combination of these physical parameters [123, 143-145]. The primary advantage of the single bath technique is that the substrate always remains in the electrolyte and no substrate transfer is necessary, hence the risk of bath contamination as well as the risk of forming an oxide layer on the cathode surface are eliminated. For the electrodeposition of nano-structured multilayers, the use of a single electrolyte is in effect a practical requirement.

Deposition of CMM coatings from a single electrolyte was first described by Brenner [145] in 1949. Alternate layers of Cu/Bi-Cu with a layer spacing in the 100nm range were obtained by automatic switching of the applied current density between two widely separated values. The deposit was cross-sectioned and etched to form a small X-ray diffraction grating. Much later the deposition of CMM Ag/Pd coatings using the single bath technique, was investigated by Cohen et al. [137], who evaluated the layered structure composed of relatively thick layers of Ag-Pd alloy rich in Ag, alternating with thin layers rich in Pd. This system was intended to take advantage of the wear resistance of multilayered materials for electrical contact applications. However, it may be worth noting that most of the interest in the electrochemical synthesis of CMM coatings using the single bath technique is centred around two alloy systems, i.e. Cu/Ni and Cu/Co for their Giant Magnetoresistive behaviours [124-125, 139-140] or their enhanced mechanical properties [143-144, 147]. The successful fabrication of multilayered coatings of Cu/Cu_{10}Ni_{90} with discrete ultrathin layers (0.9-200nm) [147] has demonstrated that the single bath electrodeposition technique is a viable approach for the production of CMM coatings.

5.2.2.1 Electrochemical fundamentals of the SBT

The cathodic polarisation behaviour of a single alloy electrolyte containing ions of two different metals, each of which is capable of undergoing electrochemical reduction with metal deposition is schematically illustrated in Figure 5.3. It is obvious that, at a potential, $E'$, which corresponds to the deposition of the more positive metal A, but is at the same time more positive than the equilibrium potential for the deposition of the other metal B (i.e. $E_A^0 > E' > E_B^0$), there is deposited pure metal A only (in the absence of the underpotential deposition of metal B). In the region more negative than the equilibrium potential of metal B (i.e. $E' < E_B^0$), an alloy of A and B is deposited. This characteristic
of the two components in a common electrolyte makes it feasible to obtain not only alloys of these metals at constant potentials or current densities, but also a successive deposition of layers of different composition by switching the applied potential or current density between two separate values.

On this basis, there are conditions which must be satisfied for the deposition of acceptable CMM coatings from a single electrolyte, these include:

- There must exist a significant difference in the deposition potentials for the two components which build up the layered structure for adequate separation of the deposition reactions. This requirement is somehow contrary to the requirement for the deposition of a structurally homogeneous alloy. Voltammetric evaluation of the bimetallic electrolyte would provide the mechanistic and kinetic information of electrode reactions necessary for the selection of compatible metal pairs and the design of an optimum process. According to Menezes et al. [147] and Tench et al. [143], the difference in the deposition potentials must be at least 0.1 V. Note that if the potential difference is too large, it is likely that during the early stage of the deposition of the more noble metal component, significant dissolution or passivation of the less noble metal substrate may occur, which will complicate the electroplating process. Under such circumstances, the deposition reaction of the less noble metal must be sufficiently irreversible so as to prevent its dissolution during the initial stage of deposition of the more noble metal onto it. As an example, the irreversibility of the Ni/Ni\(^{2+}\) reaction in the sulfamate bath has enabled the deposition of Cu/Ni CMM coatings with ease [147]. Otherwise, some other strategies must be employed to deal with this problem. A rather challenging system for production of nano-multilayers was iron-copper [148]. It was found that due to the slow coverage of copper on iron, the iron layer was left exposed to the electrolyte long enough to be anodically oxidised and dissolved during the more positive potential applied for the deposition of copper. The dissolution of the less noble iron layers was overcome by various approaches such as, addition of chloride to stifle iron dissolution in the active range of potential [149] (although it is normally found that chloride ions accelerate the corrosion of iron); addition of brighteners to improve the lateral growth of the copper layer on the iron layer [150]. However, the most effective method to avoid the dissolution of the less noble component is to start the deposition of the noble layer at a potential near the
equilibrium potential for the less noble metal and the potential was then shifted to a more positive value once the coverage of the noble metal is complete [149]. Nevertheless, a theoretical analysis by Roy [151] has shown that the dissolution and the consequent displacement reaction can be intelligently exploited to produce compositionally modulated alloys.

- In nature the CMM coatings obtained using the single bath technique belong to the metal/alloy system. In order to obtain CMM coatings of the noble metal and the alloys rich in the less noble metal (e.g. 95-98% pure with the noble component as an impurity), very small quantities of the more noble metal (typically 0.004-0.009M [147, 148]) and a high concentration of the less noble metal are required. Menezes et al. [147] have shown that nodular deposits were obtained when the Cu concentration in the electrolyte was > 10 mM; when the Cu concentration was too low (<2mM), the deposits obtained was black and powdery due to the formation of an alloy or a diffuse interface. Due to the low concentration of the more noble component in the electrolyte, the overall deposition rate for the single bath electrolyte is also slow.

5.2.2.2 Single current pulse regime

The deposition of CMM coatings from a single electrolyte is usually based on a pulse electroplating process. Gamburg [120] presented several basic types of pulsed modes which can be adopted to achieve the desired composition modulation. One of these modes is the single current pulse regime. In this regime, the designed current program consists of a train of single current galvanostatic pulses with a magnitude higher than the limiting current density of the more noble component in the electrolyte, repeating the number of times corresponding to the number of layers desired.

The single current pulse regime is best suitable for the regular alloy codeposition system. For such an alloy codeposition system, the more noble metal is first deposited upon imposing galvanostatic pulses until its ions are depleted in the cathode diffusion layer and the rate of its deposition becomes limited by ionic diffusion from the bulk solution and hence concentration polarisation occurs and results in codeposition of the less noble metal. In other words, the desired thickness of the more noble metal sublayer is reached at the transition time $\tau$, and the rest of the on-time is dedicated to the deposition of alloy
sublayers to the corresponding specification. After termination of the cathodic pulse, the concentration of the metal ions restore to the initial values at the end of the off-time. The entire cycle is then repeated. The potential response and the corresponding partial current distribution during the deposition of CMM coatings using the single current pulse regime are illustrated in Figure 5.4, with or without taking into consideration the dissolution of the less noble metal during the off-time. One disadvantage of the single current pulse regime is that the interface between the pure metal layer and the subsequent alloy layer is not sharp.

In addition, the control of the thickness and composition of individual layers is difficult. The theoretical modes [120, 140, 151] for the calculation of the thickness of both layers, the composition of the alloy layers, as well as the time needed for virtually complete restoration of the original concentration of the more noble component have been established by different authors and were applied to the electrodeposition of Cu/Pb and Cu/Ni multilayer coatings by Despić et al. [142] and the electrodeposition of Cu/Ni superlattice by Roy [151].

5.2.2.3 Double current/potential pulse regime

The dual current/potential pulse regime has much more freedom in the control of the thickness and the composition of individual layers in a CMM coating, with comparison to the single current pulse regime, as the electrical parameters can be set independently [137, 143, 147]. In this regime, the more noble metal is deposited at a current density \( j_{M1} \) below its limiting current density for a period of time \( t_{M1} \), and the current density is then switched to the current density \( j_{M2} \), at which the deposition of the less noble metal dominates, for a period of time \( t_{M2} \). Similarly the layered structure can also be obtained by using the potential as the parameters of modulation, which include \( E_{M1}, t_{M1}; E_{M2}, t_{M2} \).

For a given electroplating system, the thickness of each individual layer is determined by the time-integrated current (charge) and the corresponding current efficiency. The composition of the alloy sublayers is determined by the current/potential amplitude \( (J_{M2}/E_{M2}) \) and other electroplating conditions.

Some electroplating parameters for a few typical processes for the deposition of Cu/Ni CMM coatings are summarised in Table 5.2. For all of these deposition process the
cathode was rotated at a certain speed (300-750 rpm) during the deposition of the more noble metal, so as to improve its deposition rate and also maintain stable hydrodynamic conditions [143]. Due to the different hydrodynamic conditions for the deposition of the two components, some waiting periods, e.g. 2-3s delay with/without electrode rotation before the on-set of the deposition of each individual layer [143], were required either to allow establishment of the steady-state hydrodynamic conditions and ensure an adequate concentration of the more noble metal ions at the cathode surface, or to allow the solution to become quiescent before the electroplating of the less noble metal. It was also found by Lashmore et al. [153] that the introduction of short periods of waiting time after the high current pulse may sharpen the transition substantially and lead to the production of good quality multilayers. Instead of using the zero current during the waiting periods after the high current pulse, Hosokawa et al. [154] applied an adequate anodic current pulse. It was claimed that smoother uniform deposits were obtained.

Table 5.2

Typical electrodeposition parameters used in the fabrication of Cu/Ni multilayers.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Current/Potential regime</th>
<th>Cathode rotation (rpm)</th>
<th>Overall deposit thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tench &amp; White 1984 [144]</td>
<td>Cu -0.2 V vs SCE, Ni(Cu) -1.75 V vs SCE</td>
<td>Cu 300, Ni(Cu) 60</td>
<td>50</td>
</tr>
<tr>
<td>Menezes &amp; Anderson 1990 [147]</td>
<td>Cu -1.5 mA/cm², Ni(Cu) -90 mA/cm²</td>
<td>Cu 600, Ni(Cu) 60</td>
<td>25-50</td>
</tr>
<tr>
<td>Tench &amp; White 1991 [152]</td>
<td>Cu -0.14 V vs SCE, Ni(Cu) -105 mA/cm²</td>
<td>Cu 750, Ni(Cu) 0</td>
<td>50</td>
</tr>
</tbody>
</table>

5.3 Properties of interest of CMM coatings

In the literature, there is a wealth of experimental evidence indicating that CMM coatings may behave as 'new materials' with unique and remarkable properties not obtainable in
normal metals and alloys. Table 5.3 gives some examples of the enhanced properties of CMM coatings obtained by electrodeposition techniques. However, in the following sections this review will mainly concentrate on two aspects of particular interest, i.e. the tribological properties and the corrosion resistance of CMM coatings, which are important for the service life of plain bearings as described in Section 2.3.

5.3.1 Tribological properties

5.3.1.1 Fatigue strength

Stoudt et al. [161-162] studied the influence of a 5 μm thick Cu/Ni multilayer coating (on copper substrate) with a 1:1 layer thickness ratio and a composition modulation wavelength (bilayer repeat length) of 40 nm, on the fatigue crack nucleation during the rotating beam fatigue testing. It was found that in contrast to the monolithic Cu and Ni coatings, which has no numerically significant influence on the observed fatigue lives, the Cu/Ni multilayer coating resulted in a dramatic improvement in the fatigue crack initiation resistance of the copper substrate. SEM examination of the multilayer coated surface after fatigue testing revealed that the quantity and magnitude of the slip steps on the surface were substantially smaller than those observed on the monolithic Cu or Ni-coated surfaces, and also that there were no indications that the multilayer coating fractured in a fashion similar to that observed for the monolithic Ni-coated samples. It was then claimed that the enhanced hardness and resulting toughness produced by nanometre-scale layering of two ductile constituent materials was the most likely source of the slip suppression and homogeneous deformation that prevented fatigue crack nucleation through the normal surface roughening mechanisms in these samples. Meanwhile, the likelihood of crack initiation by secondary mechanisms (i.e. brittle cracking, delamination and cyclic softening of the coating) may be substantially reduced for the multilayer coated samples due to the capacity of these coatings to deform when the substrate strains reach the critical levels. The retained toughness of the sublayers from the parent materials, the high density of interfaces that form a barrier to slip and help to disperse it near the surface, and the presence of any residual compressive stress in the electrodeposited multilayer coatings were thought to be responsible for the observed resistance to secondary fatigue crack initiation with the Cu/Ni multilayer.
Table 5.3 Examples of enhanced properties of CMM electrodeposits

<table>
<thead>
<tr>
<th>Enhanced properties</th>
<th>Alloy system</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| Tensile properties  | Cu/Ni [143, 144, 147, 152, 155] | – Tensile strength peaks at 1900MPa and a layer spacing of 20 nm (2nm Cu-18nm Ni) [147]
|                     | Ni/Sn [156] | – Dependence of the yield strength on the layer spacing follows the Hall-Petch relation [156]
|                     | Cu/Ag [157] | – Enhancement was attributed to the pinning of dislocations at the coherent interfaces of the layered structure [143, 147, 156, 157]
|                     |             | – Loss of coherence at interfaces at thicker layer spacings and the development of discontinuous copper layers at very small layer thicknesses lead to the decrease in the tensile strength [158]
|                     |             | – Refinement of grains in the Cu layers also contributes to the tensile strength enhancement [157]
|                     |             | – Formation of nodular layers is responsible for the brittleness of the multilayer coatings [155]
| Giant magnetoresistance (GMR) | Cu/Co [124, 140, 158] Cu/Ni [125, 158, 159] | – A dramatic drop of the electrical resistivity in a magnetic field [160]
|                     |             | – 55% GMR for electrodeposited Cu/Co multilayers having 800 to 6000 layers [158]
|                     |             | – The magnitude of GMR effect is related to the nonmagnetic Cu layer thickness [158], and the ratio of the individual layers [159]
| Tribological properties | Cu/Ni [161-163], Ni/Sn [164] Ni-P/Sn [126], Ni-P/Cu [165] | See Section 5.3.1
| Corrosion resistance | Zn/Ni [121-122, 166], Zn/Co [167-168], Zn/Zn-Fe [123, 169-170] | See Section 5.3.2
5.3.1.2 Wear resistance

The wear resistance of CMM coatings has been studied by a number of researchers. Ruff and Lashmore [163] reported that for the electrodeposited Cu/Ni multilayer coatings, the most wear-resistant coating was the one having the smallest layer spacing, 3.8 nm. The multilayer structure in these coatings was thought to provide internal barriers to wear which occurred by plastic deformation processes, and the individual layer spacing determined the level of stress necessary to initiate severe wear. The tribological properties of multilayered Cu/Ni-P coatings, prepared using a single bath technique, was studied by Miyke et al. [165]. It was stated that the wear resistance of the multilayered coating is superior to that of Ni-P single layer coatings. The enhancement was attributed to the suppression of the propagation of cracks in the multilayered structure.

Wang and Singh [164] studied the coefficient of friction and the wear rate of Ni/Sn multilayer coatings by pin-on-disk and block-on-ring tests. They suggested that the soft tin acted as a solid lubricant between the contacting surfaces, and the wear resistance of the multilayer coatings greatly depended on the thickness, area coverage, composition, and stability of the interface tin-rich film. Samples with a lower tin content and/or a thinner layer spacing exhibited enhanced wear resistance compared to those with a higher tin content and/or thicker layers. The improvement was attributed to both the solid-lubricating effect of the tin and the enhanced mechanical properties of the multilayered coatings.

5.3.2 Corrosion resistance

In recent years there has been an increased interest in the electrodeposition of zinc alloy CMM coatings due to their superior corrosion resistance. Kalantray et al. [121] prepared alternate layers of zinc and nickel (each of 1, 2, or 4 μm thickness, with an overall thickness of 8 μm) on a steel substrate using the dual bath technique. It was found that the corrosion performance of these multilayered coatings in a 5% neutral salt spray was better than that of a single layer zinc deposit, and the salt spray resistance measured by the area percentage of red rust after a given time increased as the number of individual layers was increased. The enhancement of corrosion performance was attributed to the grain refinement effect and the reduced activity of the multilayered coatings, which was
indicated by the less negative corrosion potential as the number of layers increased. Similar results were also obtained by Ivanov et al. [166], who characterised the corrosion resistance of Zn/Ni CMM coatings by corrosion potential measurement. The corrosion potentials of Zn/Ni CMM coatings (ending with a Zn oversublayer and a total thickness of 8-9 µm) with a great number thin sublayers (0.7 µm), were more positive (0.150-0.200 V) than the potentials of CMM coatings with a few thick sublayers (3.0 µm). The most positive corrosion potentials (-0.75/-0.8 V relative to a mercury sulfate reference electrode) was found with the CMM coatings with a Ni oversublayer, which were thus thought to be the most corrosion resistant.

Chawa et al. [122] made a successful attempt to electrodeposit layered coatings of zinc and zinc-nickel alloy with a nominal composition of 12 wt.% nickel. They claimed that the optimum layer configuration of those test samples appeared to be the four layer Zn-Ni/Zn, which had a time of 552 hours to the first appearance of red rust, as compared with 197 hours for pure zinc coatings and 313 hours for single layer Zn-Ni alloys. Their results also suggested that it is difficult to use the results of short-term electrochemical tests, e.g. the measurement of corrosion potential and corrosion current, to predict the sacrificial corrosion protection capability of CMM coatings.

Kirilova et al. [167-168] reported the deposition and the corrosion behaviour of Zn/Co (from a dual bath) and Zn-6.5%Co/Zn-1%Co alloy (from a single bath) CMM coatings. It was claimed that the best corrosion resistance with regard to the appearance of white rust was observed for the multilayer coatings chromated for 20 seconds and consisting of four sublayers, each 3.0 µm thick, deposited from a single bath. For both Zn/Co and Zn-6.5%Co/Zn-1%Co alloy CMM coatings chromated for 20 seconds no red rust appeared on their surface even after 1584 hours of salt spray corrosion test. In agreement with the result reported by Chawa et al. [122], it was also found that the chromated CMM coatings of 40 sublayers with 0.3 µm individual layer thickness were less corrosion resistant than those with a 3.0 µm individual layer thickness.

Parallel studies on the electrodeposition of Zn/Fe CMM coatings from a dual bath and Zn-(5-20 wt.%)Fe/Zn-(50-75 wt.%)Fe [123, 169-170] alloy CMM coatings from a single bath have been carried out at Loughborough University. The reason for the interest in Zn-Fe
alloy system is that Zn-Fe alloy not only offers improved cathodic protection of mild steel compared to pure zinc (15-20 wt.% Fe) [171], it can also offer better weldability and paintability (60-80 wt.% Fe) [172]. SEM examination has shown that the multilayer structure developed was satisfactory, however, the characterisation of the corrosion behaviour of those multilayer coatings has not been carried out yet.
6 Experimental techniques

6.1 Introduction

Experimental work carried out in this research has been divided into four major categories:

- Establishing a suitable sulfate/gluconate electrolyte and the optimum electroplating conditions, from which pure tin and Sn-Co alloy coatings could be deposited from two separate current density ranges. The electrodeposition was conducted under both direct and pulsed current conditions.

- Electrodeposition of compositionally modulated Sn-Co alloy multilayer coatings on plain bearings as overlays, the fatigue strengths of which were subsequently assessed.

- Electrochemical characterisation of the electrolyte, to understand the codeposition behaviour of tin and cobalt.

- SEM observations (surface morphology and cross-section) of the Sn-Co alloy multilayer coatings in the as-plated state and after fatigue tests.

With respect to the electrolyte development, the desired current density-deposit composition relationship expected for a potential solution is schematically shown in Figure 6.1 (the solid line, or less probably the dotted line). Under these ideal conditions, satisfactory pure tin deposits and Sn-Co alloy deposits containing approximately 20% cobalt, respectively, should be able to be deposited by varying the applied current density only. In another words, there should be two wide current density windows. One is at the lower current density end, and the other at the higher current density end. This is the basis for the electrodeposition of compositionally modulated alloy multilayer coatings using the single bath technique. This feature was thus used later as one of the criteria on deciding whether an electrolyte was suitable for the deposition of compositionally modulated Sn-Co alloy multilayer coatings.
6.2 General procedure

6.2.1 Electrode materials and pretreatment

Stainless steel EN58B strip was used as the anode. The anode strip was masked with chemically inert tape (3M Scotch 8403) to give a one-sided active surface area of 90×72 mm. The copper sheet of 0.25mm thickness was cut into 50×50 mm panels to be used as cathodes. The back of the cathodes was masked with either the chemically inert tape or Lacomit varnish. The effective surface area for electrodeposition was about 25 cm².

Prior to electroplating, copper panels were pickled in 50% (v/v) S.G 1.42 nitric acid for 10–20 seconds, followed by rinsing thoroughly in tap water, and then in deionised water. After that, the panels, masked with chemically inert tape, were rinsed with acetone and dried with hot air. Those masked with Lacomit varnish were dried directly with hot air. Rinsing with the acetone was found to dissolve the varnish mask away.

6.2.2 Heating and agitation

The agitation method affects the way by which the electrolyte was heated. In this research, magnetic stirring was normally applied when agitation was considered. With magnetic agitation, the solution was heated by the hotplate with a temperature control accuracy of ± 3°C. The agitation level was rated by 10 divisions marked on the hotplate control, with the strongest agitation effect at level 10.

When no agitation was applied and the solution was used under a static condition, the electrolyte was heated using a 25 litre water bath so as to have more accurate and stable temperature control(± 1°C) than heating with a hotplate.
6.2.3 Morphology and composition

The surface morphology and the cross-section of the deposits were examined using a Cambridge 360 scanning electron microscope (SEM), or a Leo 1530VP Field Emission Gun scanning electron microscope (FEG-SEM). The composition of the deposits were analysed with an energy dispersive X-ray spectrometer (EDX) coupled to the SEM.

6.2.4 Cathodic current efficiency

After electrodeposition, the pre-weighed plated samples were rinsed with running tap water, deionised water, and finally with acetone, before being dried in a hot air stream. The dried samples were weighed again to obtain the weight gain under each electrodeposition condition. The cathode current efficiency (CCE) was calculated with the following equation:

\[
CCE = \frac{\Delta W(C_{Co}/M_{Co} + C_{Sn}/M_{Sn}) \times 2F}{jAt} \times 100\% \quad (6.1)
\]

where

- \(CCE\) cathode current density
- \(\Delta W\) weight gain after electroplating (g)
- \(C_{Co}, C_{Sn}\) weight percentage of cobalt, or tin in the deposit
  \(C_{Co} + C_{Sn} = 100\%\)
- \(M_{Co}, M_{Sn}\) atomic weight of cobalt, and tin (g/mol)
- \(F\) faraday constant (96485 coulomb/mol)
- \(j\) applied current density (A/dm²)
- \(A\) effective cathode surface area (dm²)
- \(t\) electroplating duration (second)

The cathode current efficiency could also be calculated by the measurement of the actual thickness of the deposit on the cross-section of the sample, using the following equation,

\[
CCE = \frac{2 \times 10^{-2} F \rho T(C_{Co}/M_{Co} + C_{Sn}/M_{Sn}) \times 100\%}{jt} \quad (6.2)
\]

where \(\rho\) density of Sn-Co alloys (g/cm³),
\[
\frac{1}{\rho} = \frac{C_{Sn}}{\rho_{Sn}} + \frac{C_{Co}}{\rho_{Co}}
\]
\[
\rho_{Sn} = 7.30g/cm^3, \quad \rho_{Co} = 8.71g/cm^3
\]

\( T \) measured thickness of the deposit (\( \mu \text{m} \)), \( C_{Co}, C_{Sn} \) weight percentage of cobalt, and tin in the deposit (\( C_{Co} + C_{Sn} = 100\% \)), \( M_{Co}, M_{Sn} \) atomic weight of cobalt, or tin (\( \text{g/mol} \)), \( F \) faraday constant (96485 coulomb/mol), \( j \) applied current density (\( \text{A/dm}^2 \)), \( t \) electroplating duration (second).

### 6.3 Evaluation of ACHROLYTE electrolyte

Initially, a commercial electrolyte, ACHROLYTE, was evaluated first in terms of the deposit composition-current density relationship, the deposit surface quality, the cathode current efficiency in the recommended current density range, and the solution stability.

#### 6.3.1 Bath Preparation and operating conditions

Bath preparation of the ACHROLYTE electrolyte involved dissolving two ingredients, ACHROLYTE A and ACHROLYTE B, in deionised water. ACHROLYTE A and ACHROLYTE B were supplied in solid form. For one litre of the working solution the following quantities of ACHROLYTE A and B were required:

- ACHROLYTE A 40 g
- ACHROLYTE B 5.0 g

A 5 litre glass beaker was about half filled with deionised water. The appropriate quantities of ACHROLYTE A and B powder were then slowly added into the water with sufficient agitation. After complete dissolution of the agents, the solution was filtered in order to remove the insoluble species precipitated at the bottom of the beaker. The pH value of the solution was adjusted to 8.2 (8.0–8.6) with sodium hydroxide (10% solution). The solution was finally made up to 5 litres in a volumetric flask. The composition of the ACHROLYTE solution thus prepared is given in Table 6.1. During the whole electroplating process, appropriate magnetic stirring was applied and the electroplating temperature was maintained at approximately 45°C.
### Table 6.1 ACHROLYTE solution composition

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantity of ingredients g/l</th>
<th>Composition of ingredients %</th>
<th>Composition of the electrolyte g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACHROLYTE A</td>
<td>40</td>
<td>10-30%</td>
<td>4.2-12.5</td>
</tr>
<tr>
<td>ACHROLYTE B</td>
<td>5</td>
<td>5-10%</td>
<td>3.4-7.0</td>
</tr>
</tbody>
</table>

### 6.4 Development of a new electrolyte

#### 6.4.1 Electrolyte preparation

The modified sulfate/gluconate bath composition and the electroplating parameters are shown in Table 6.2. For each experiment, one litre of the solution was freshly prepared with deionised water and kept standing for 24 hours before electroplating. All chemicals used were general purpose regents.

<table>
<thead>
<tr>
<th>Table 6.2 Modified sulfate/gluconate bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSO₄</td>
</tr>
<tr>
<td>CoSO₄·7H₂O</td>
</tr>
<tr>
<td>Sodium gluconate</td>
</tr>
<tr>
<td>Na₂SO₄·10H₂O</td>
</tr>
<tr>
<td>Gelatine</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Agitation</td>
</tr>
</tbody>
</table>

The electroplating beaker was approximately two thirds filled with deionised water. The complexing agent, sodium gluconate, was then added with magnetic stirrer agitation. After it was completely dissolved the stannous sulfate was then slowly added, followed by the addition of cobalt sulfate and sodium sulfate. Agitation was maintained for 1-2 hours to
ensure the complete dissolution of all the soluble constituents. The solution was filtered to remove the insoluble tin oxide before the pH adjustment. The pH value of the filtered solution was adjusted to the specified value with 10% sodium hydroxide solution or 10% (v/v) S.G 1.84 sulphuric acid. The appropriate quantity of gelatine was dissolved in a small amount of warm water in advance and then was added into the solution. Finally the solution was made up to the correct working volume.

### 6.4.2 Organic addition agents

The organic addition agents used in this research include gelatine and Tween 20. Both of them were used as received. The chemical name for Tween 20 is polyethylene oxide (20) sorbitan monolaurate. It is a non-ionic surfactant with a structure as follows:

![Chemical structure of Tween 20](image)

\[ x + y + z + w = 20 \]

\[ \text{Tween 20, } R = \text{CH}_2(\text{CH}_2)_{10}\text{CH}_3 \]

### 6.4.3 Hull cell test

The standard 267-ml Hull cell was used to carry out the qualitative assessment of the effectiveness of the organic additives in eliminating the dendrites on the surface of the tin-cobalt alloy deposits. The solution to be tested had the composition given in Table 6.2 except for the addition agents. The solution was preheated to 50°C before it was transferred into the Hull cell which was stood in a water bath at the temperature of 45°C. After the temperature of the solution in the testing cell came to an equilibrium at about 45°C, the experiment was started.

The anode panel was EN58B stainless steel. The cathode panels were 65×102 mm copper, which were masked on one side with chemically inert tape and were pre-treated as
described in section 6.2.1. The Hull cell test was carried out under the condition of a constant current of 2 A and an electroplating time of 10 minutes. The current density distribution along the mid-height line of the cathode panel was calculated using the following formula [173]:

\[ j_L = I_{\text{cell}}(5.10 - 5.24 \log L) \]  

(6.4)

where \( j_L \) is the current density (A/dm\(^2\)) at a distance \( L \) (cm) from the high current density end of the cathode panel; and \( I_{\text{cell}} \) (A) is the cell current employed.

6.5 Pulse electroplating of tin-cobalt alloys

6.5.1 Introduction

In the direct current electroplating of tin-cobalt alloys, one major problem was that tin-cobalt alloys were prone to form dendrites. Normally, dendritic growth of coatings is overcome by the addition of additives. However, it was usually difficult to identify a suitable additive. In this research, pulsed current was used to achieve this purpose because inhibition of dendrites has been established as one of the advantages of pulsed current electroplating.

The pulsed current in all of the experiments had a unipolar square waveform (see Figure 4.2(a)). A 25V/20A Axel Åkerman CAPP-25/20-K rectifier with associated software and controlling PC was used to produce the desired pulse waveform. The connecting wire from the pulse rectifier to the electroplating bath was twisted together in the way suggested in the reference [174] so as to minimise the inductive effect of the system, avoiding the degradation of the pulse rise time.

6.5.2 Pulse electroplating trial

As a trial, three different square waveforms were examined. The on-time for all these waveforms was 1 millisecond, which is the limit of the pulse electroplating unit. The off-times for these waveforms were 4, 9, and 19 milliseconds, respectively. The corresponding duty cycles were 20%, 10%, and 5%. The deposit thickness under each condition was
expected to be 8-10 microns. The electrolyte and the operating conditions in this experiment are given in Table 6.3. The solution was concentrated and had two addition agents included. The temperature of the solution was maintained at about 55°C.

Table 6.3 Electrolyte for pulse electroplating trial

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSO₄</td>
<td>36g/l</td>
</tr>
<tr>
<td>CoSO₄·7H₂O</td>
<td>24g/l</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>120g/l</td>
</tr>
<tr>
<td>Na₂SO₄·10H₂O</td>
<td>20g/l</td>
</tr>
<tr>
<td>Gelatine</td>
<td>2g/l</td>
</tr>
<tr>
<td>Tween 20</td>
<td>4ml/l</td>
</tr>
<tr>
<td>pH</td>
<td>4.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>55°C</td>
</tr>
<tr>
<td>Agitation</td>
<td>none</td>
</tr>
</tbody>
</table>

6.5.3 Hull cell test

The Hull cell test under pulsed current conditions was carried out in a similar way as that under direct current conditions (See Section 6.4.3). The pulsed current waveforms used for these tests were designed according to such a standard that the average current flowing through the cell for all of the pulsed waveforms was always 1 A. The electroplating duration was 5 minutes. The anode and the cathode were EN58B stainless steel and copper, respectively, which were pre-treated as in Section 6.2.1. The electrolyte for these tests is given in Table 6.4.

6.5.4 Cloud point of Tween 20

The effect of the constituents making up the sulfate/gluconate electrolyte on the cloud point of the solution added with Tween 20 was therefore studied. For each experiment, 300 ml solution was prepared. The solution was heated slowly and agitated with a magnetic stirrer until it became cloudy. The solution was then removed from heat and cooled down until it was clear again. The temperature of the solution was measured with a thermometer.
The cloud point was taken as the average value of the temperature when the solution became cloudy on heating and that when the solution became clear again on cooling.

| Table 6.4 Electrolyte for Hull cell tests under pulsed current conditions |
|-----------------------------|----------------|
| SnSO₄                       | 36g/l          |
| CoSO₄·7H₂O                  | 24g/l          |
| Sodium gluconate            | 120g/l         |
| Na₂SO₄·10H₂O                | 20g/l          |
| Boric acid                  | 30g/l          |
| Tween 20                    | 1~7ml/l        |
| pH                          | 4.0            |
| Temperature                 | 45~50°C        |

6.5.5 Phase identification

The phases in tin-cobalt alloy electrodeposits were identified by X-ray diffractometry (Bruker D8 X-ray diffractometer). The X-ray diffraction pattern was recorded with Cu Kα (λ=1.5406Å) irradiation in the 20 angular range of 25° to 100°. The scan rate was 0.02°/sec. These patterns were then indexed using the Powder Diffraction Files (PDF) published by the JCPDS-International Centre for Diffraction Data.

6.5.6 AES Depth profiling

Auger Electron Spectroscopy (AES) depth profiling was performed with a Jeol JAMP7100 spectrometer. A primary electron beam current of 0.5×10⁻⁶A at 20 keV was employed. Depth profiling was carried out by combining AES with sequential argon-ion bombardment. The ion-beam energy was 3 keV and a defocused beam was rastered to give a current density of 50 ×10⁻⁶ A/cm². The sputter rate was 12×10⁻⁹ m/min for these conditions. Quantification was carried out using SnO₂ and Co₃O₄ reference materials. Depth scale calibration was using a theoretically-derived etch rate.
6.6 Compositionally modulated tin-cobalt alloy multilayer coatings

Compositionally modulated tin-cobalt alloy multilayer coatings were electrodeposited on the surface of both copper panels and plain bearings. The effect of the thickness and composition of individual layers on the properties of the multilayer coatings obtained was investigated. The multilayer coating was developed as a plain bearing overlay, therefore the most important mechanical property of concern was the fatigue strength. Other properties including the microhardness, the ductility and the internal stress of the deposit, which are related to the fatigue strength, were also studied.

6.6.1 Electrodeposition of multilayer coatings

The pulse sequence for the electrodeposition of compositionally modulated Sn-Co alloy multilayer coatings is schematically shown in Figure 6.2. Sn-Co alloy layers were deposited under either direct or pulsed current conditions at an average current density of 3 A/dm², whereas pure tin layers were always deposited using direct current at a current density of 0.5 A/dm².

For the electrodeposition of multilayer coatings on copper substrates, the pre-treatment was the same as previously described. During electroplating, the copper substrate was moved reciprocally in the solution (5 litres). The horizontal stroke was about 2-3cm, and the speed was about 25 cycles per minute. The purpose of introducing slight reciprocal agitation was to prevent localised ion depletion, and also to dislodge hydrogen gas bubbles from the deposit surface avoiding the formation of streaks.

Electrodeposition of tin-cobalt alloy multilayer coatings on plain bearings was carried out with two types of plain bearings supplied by Dana Glacier Co. Ltd., i.e. the copper-lead alloy (or the bronze) bearing and the aluminium-based alloy bearing. The latter had been pre-electroplated with a 1-3μm nickel barrier. A special electroplating jig (Figure 6.3), also supplied by Dana Glacier Co. Ltd., was used to hold the bearings and to produce a uniform
current distribution during Sn-Co electrodeposition. Figure 6.3 also shows the bearing arrangement in the electroplating jig.

Prior to electroplating, the bearings were degreased in trichloroethylene at about 50°C for 1 minute. This process was then repeated once more with clean solvent. The second wash in clean solvent should produce very clean parts. The bearings were then rinsed thoroughly in running tap water and deionised water in succession. The bronze bearings were immersed in 60% (v/v) S.G. 1.18 HCl at room temperature for 1 minute. The aluminium-based alloy bearings (with nickel barrier) were immersed in 5% (v/v) S.G 1.84 sulphuric acid at room temperature for 1 minute. Thorough rinsing then followed. After mounting in the electroplating jig, all the bearings were finally electroplated with a multilayer overlay of approximately 13-16 microns for property assessment.

6.6.2 Cross-section preparation

For the microscopic examination of the multilayer coating, the electroplated sample was sectioned and mounted in conductive resin. After grinding to 1200 grit waterproof abrasive paper, the mounted section was polished with diamond paste of 6μm and 1μm, respectively. The polished sample was then etched in acidic ferric chloride solution for 5-10 seconds to reveal the thickness configuration of the multilayer coating. The etchant consists of 5g ferric chloride, and 50 ml hydrochloric acid in 100 ml deionised water. It could be further diluted with water in order to reduce the etching speed making the process more controllable.

Note that for the examination of bearings after fatigue testing, the sectioned sample was first plated with a thin layer of electroless nickel deposit. It was then electroplated with a thick layer of copper from an acidic copper sulfate solution. The purpose of this pre-treatment was to prevent the fatigue cracks from damage during the cross-section preparation.

6.6.3 Microhardness

Microhardness of single layer tin or tin-cobalt alloy coatings on copper substrate was measured using a Reichart microhardness tester and MeF2 microscope combination. The
thickness of the deposits was typically 10-15 μm. In all microhardness work, an applied load of 5g was used for deposits of pure tin, while both 5g and 10g was applied for tin-cobalt alloy deposits of higher cobalt content. A series of three indentations was made over each specimen and the average value reported. Microhardness was calculated from:

\[ HV = 1854.4 \frac{P}{d^2} \text{ (kg mm}^{-2} \text{)} \]  \hspace{1cm} (6.5)

where \( P \) is the applied load (g), and \( d \) is the diagonal of indentation (μm).

The surface morphology of tin and tin-cobalt alloy deposits was pyramidal and nodular, respectively. Therefore no regular indentation was obtainable on the surface. In this situation, microhardness was measured on the cross-section of the samples. Before cross-section preparation, the samples were plated with a protective copper deposit from an acidic copper sulfate electrolyte. The samples were immersed in the solution with the current switched on so as to prevent the reduction of copper from the solution by the displacement reaction.

### 6.6.4 Internal stress

The internal (or residual) stress in the single or multilayer tin-cobalt alloy coatings was determined using the bending strip method [175]. As shown in Figure 6.4, it consists of a copper strip and a supporting jig made of plastic. The size of the copper strip used in this experiment was 100×10×0.25mm.

The copper panel was insulated on one side with Lacomit varnish and was electroplated on the other side facing the anode. The bottom end of the strip was fixed in the jig and connected to the negative terminal of a power supply, while its upper end was free to deflect.

The plated strip bends due to the internal stress in the electrodeposits. The nature of the internal stress in the deposit is tensile or contractive if the strip bends towards the anode. In contrast, the internal stress is compressive or expansive if the strip bends in the opposite direction.
To determine the magnitude of the internal stress, the deflection of the free end was measured using a ruler (with a smallest graduation of 0.5 mm) after the jig was withdrawn from the electrolyte. On the basis of the measured deflection of the free end, the stress value corresponding to a specific thickness of the deposit was calculated according to the Stoney equation [175],

$$\sigma = \frac{E(T^2 + Lt)\delta}{3L't}$$

(6.5)

where: $\sigma$ is the internal stress in MPa, $E$ is the modulus of elasticity of the copper substrate, which is 130GPa, $T$ is the thickness of the copper strip in mm, $\delta$ is the deflection of the free end in mm, $L$ is the length of the strip deposited with tin-cobalt alloy coatings in mm, $t$ is the thickness of the deposit in mm.

In order to monitor the development of internal stress with increase in the deposit thickness, a fine copper wire ($\phi$ 0.25 mm) was straightened, insulated and attached to the free end using a cyanoacrylate adhesive (Figure 6.4). The deflection of the copper wire extending out of the solution was recorded at a constant distance from the fixed end of the copper strip during the whole electroplating process. This deflection gives an indication of the nature and the comparative magnitude of the internal stress.

### 6.6.5 Fatigue strength

Fatigue tests were carried out on a Sapphire fatigue testing machine at Dana Glacier Co. Ltd. The Sapphire machine applies a cyclic sinusoidal load to the bearing. The initial load is 48 MPa. This load is then increased every 20 hours by 7MPa until fatigue cracks are observed on the surface of the bearing. The fatigue rating of the overlay is thus obtained. The testing conditions comprise a shaft speed of 2800 rev./min. and an oil temperature of 80°C.

### 6.7 Potentiodynamic polarisation studies

The cathodic potentiodynamic polarisation of the sulfate/gluconate electrolyte containing tin, cobalt, and both tin and cobalt ions, respectively, were conducted to illustrate the
electrodeposition mechanism of tin-cobalt alloys. Factors having an effect on the polarisation curves considered in this experiment include the metal ion and complexing agent concentrations, the pH value, and the agitation strength. The effect of the surfactant Tween 20 was also investigated.

The polarisation was performed in a conventional three-electrode cell using an ACM Instruments computer controlled potentiostat, model Auto Tafel HP, linked to a personal computer. 250 ml of freshly prepared solution made with deionised water was used for each test. The whole cell was placed in a water bath. Once the electrolyte acquired the specified temperature of 45°C, the electrodes were placed in the cell.

The working electrode was a copper cylinder (ø 6 mm x 5 mm) embedded in non-conductive Epofix resin. This arrangement guarantees a constant surface area of about 0.28 cm² for each run, and also avoids the problem of the insulating material peeling away from the working electrode during the test. The working electrode was ground progressively using 400, 600, 800 and 1200 grit waterproof abrasive paper, followed by pickling in 50% (v/v) S.G 1.42 nitric acid for 10-20 seconds. It was rinsed thoroughly before being transferred into the cell.

The reference electrode used was a Russell SRR5 saturated calomel electrode supplied with a salt bridge. The salt bridge consisted of a length of polymeric tube connected to a fritted glass end-piece, and was filled with saturated potassium chloride solution to provide a suitable conductive medium. The fritted glass end-piece was placed 3-5 mm away from the working electrode. The calomel electrode was held at the same height as the tip of the fritted glass end-piece of the salt bridge in the cell to reduce the head of saturated potassium chloride to a minimum, thus avoiding leakage of potassium chloride through the tip. Use of the salt bridge prevented possible poisoning of the electrode due to species formed in the test cell.

As the tip of the fritted glass end-piece of the salt bridge was some distance from the working electrode, a drop in IR was inevitable and unavoidable. However, as the conductivity of the solution was high, and small currents were employed due to the small surface area of the working electrode, the drop in IR was therefore negligible.
For the counter electrode, a sheet of platinum foil of 25 cm$^2$ (5cm x 5cm) was used. No special pre-treatment of this was carried out, except for periodic washing with hot tap water, deionised water, acetone and deionised water in sequence before each run.

Before each polarisation run, the rest potential between the working electrode and the reference electrode in open circuit was measured. The potential was then swept cathodically from the rest potential to 2V. A sweep rate of 120mV/min was employed for all the tests. The rest potential for copper substrates in the electrolyte under study was found to be within the range of –100 to –300 mV vs. SCE.
7 Results and discussion

7.1 Electrodeposition of Sn-Co alloys: Part I direct current electroplating

7.1.1 Evaluation of ACHROLYTE electrolyte

7.1.1.1 Effect of current density

With 5 litres of fresh ACHROLYTE solution, the effect of current density on the composition and surface morphology of the tin-cobalt alloy deposits was investigated. The deposit thickness obtained was expected to be approximately 2-3 microns. As shown in Figure 7.1(a), within the current density range of less than 0.5 A/dm², the cobalt content in the deposits decreases sharply with increase in the applied current density. Further increase in the current density only shows a small effect on the deposit composition. Eventually the cobalt content reaches a constant of 12-13 wt.% at current densities higher than 2A/dm². The same tendency was also found in the feasibility study by Coignard et al. [176] as shown in Figure 7.1(b).

However, the relationship between the deposit composition and the current density observed in this research is different from that reported by the process inventors, Hemsley and Roper [37]. They claimed that operation with the recommended current density range of 0.2 to 1.5 A/dm² yields deposits of relatively constant alloy composition, and the alloy deposited at 1 A/dm² under recommended conditions contains 20 wt.% cobalt and 80 wt.% tin. Only at excessively low current densities would the deposition of cobalt be favoured. This difference observed is probably due to the different agitation methods adopted in each study. According to Hemsley and Roper, for rack electroplating applications, a moving cathode bar is recommended with a movement rate of 4 to 10 metres/minute. However, in this research, a magnetic stirrer was mainly used to agitate the solution, the agitation strength of which is very difficult to quantify.
In appearance the deposit is bright when the current density is 0.1 A/dm², it becomes dull grey when the current density is varied in the range of 0.3-0.5 A/dm². Even higher current densities make the deposits dark and powdery. SEM micrographs in Figure 7.2 indicate that nodular grains dominate the surface at all current densities, but some dendrites, which are white on the micrographs, appear on the surface of the deposits when the current density is higher than 1 A/dm². These dendrites are rich in tin, and correspondingly the nodules are rich in cobalt. Therefore the practical current density for this electrolyte should not be higher than 1 A/dm².

7.1.1.2 Current efficiency
On the basis of the dependence of the deposit composition and morphology on the current density, two current densities, 0.5 and 0.62 A/dm², were chosen to obtain thicker Sn-Co alloy deposits with prolonged electroplating durations. The corresponding cathode current efficiency was calculated using Equation 6.2 through the measurement of the actual deposit thickness. The result is given in Table 7.1. Although the electroplating time was as long as 2-3 hours, the actual thickness of the deposits obtained was only 2.5-3.5 µm and meanwhile the deposits were powdery. The cathode current efficiency calculated was 8-11%.

Table 7.1 Cathode current efficiency for the commercial electrolyte

<table>
<thead>
<tr>
<th>Electroplating conditions</th>
<th>Thickness µm</th>
<th>Cobalt content wt.%</th>
<th>CCE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density A/dm²</td>
<td>Electroplating time hour</td>
<td>Expected</td>
<td>Actual</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>23</td>
<td>2.5</td>
</tr>
<tr>
<td>0.62</td>
<td>3</td>
<td>42</td>
<td>3.5</td>
</tr>
</tbody>
</table>

According to Hemsley and Roper [37], the current efficiency within the current density range of 0.1 to 0.8 A/dm² should be approximately 92%, which is much higher than the result obtained. The great discrepancy in the current efficiencies can be explained by the fact that ACHROLYTE electrolyte was originally developed to deposit coatings typically
0.25-1μm thick and the solution is dilute in metal salts (see Table 6.1). It is therefore very probable that the process becomes less efficient when it is used to deposit thicker coatings.

7.1.1.3 Solution stability

In order to study the stability of the ACHROLYTE solution, two samples were plated from 5 litres of used solution which was approximately 9 months old. The compositions of the deposits were compared with those obtained from a fresh solution. The cathode substrate used in the aged solution was copper. For the experiment with the fresh solution which was carried out by Coigniard et al.[176], a mild steel cathode electroplated with nickel was used. As shown in Table 7.2, the deposit from the 9 months old solution is mainly cobalt with a composition which is much higher than that from the fresh solution. Although there is a difference in the substrates used, a substrate, which may lead to an epitaxial growth of the deposit with a different microstructure, normally does not have such a pronounced influence on the deposit composition. Even the effect of substrate on the deposit microstructure is only observable within a very thin layer of deposits. With increase in the deposit thickness, the effect of the substrate disappears. Therefore the remarkable increase of cobalt content in the deposit from the old solution must be due to the loss of electroactive tin(II) ions as a result of the oxidation of tin(II) to tin(IV) ions in the solution. In Table 7.2, results for shorter ageing time obtained by Coigniard et al.[176] are also cited. It can be seen that the cobalt content of the deposit had more than doubled even though the solution was only 10 days old. It can therefore be concluded that the ACHROLYTE solution lacks long term stability.

Based on these results, it is apparent that the ACHROLYTE solution is not appropriate for tin-cobalt alloy multilayer electroplating. The sharp decrease of the cobalt content in the deposits in the small current density range makes the deposition of about 20% cobalt very difficult to control. The reproducibility of the process is also problematic in practice (Figure 7.1(b)). Secondly, although a constant deposit composition appears within the higher current density range of 1-4 A/dm², the deposit is powdery and unacceptable. For these reasons the desired compositional modulation is not possible from the ACHROLYTE solution by changing the current density only. Also, the surprisingly low cathode current efficiency and the stability problem associated with ACHROLYTE make it even more undesirable.
CHAPTER 7 RESULTS AND DISCUSSION

Some modifications, therefore, needed to be carried out before the ACHROLYTE solution could be used to deposit tin-cobalt alloy multilayer coatings. However, the exact composition of the proprietary ACHROLYTE solution is not known. This hinders understanding and controlling the experimental investigation. In this case a new process had to be developed, which should show a potential for the deposition of compositionally modulated tin-cobalt alloy multilayer coatings.

Table 7.2 Effect of ageing of ACHROLYTE solution on Sn-Co alloy electrodeposition

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Ageing duration</th>
<th>Electroplating conditions</th>
<th>Cobalt in deposit wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fresh [176]</td>
<td>0.5 Moving Bar 11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 months (approximately)</td>
<td>0.5 Moving Bar 88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fresh</td>
<td>0.5 Magnetic stirring 12</td>
<td></td>
</tr>
<tr>
<td>2 [176]</td>
<td>10 days (approximately)</td>
<td>0.5 Moving Bar 29</td>
<td></td>
</tr>
</tbody>
</table>

7.1.2 Development of a new electrolyte

In Rechim and co-workers’ study [44] on the effect of stannous sulfate on the electrodeposition of Sn-Co alloys from gluconate baths, it was reported that the cobalt content in the deposit at 3 A/dm² decreases with increase in the concentration of stannous sulfate. Beyond a certain concentration only tin is deposited. The variation of the cobalt content in the deposit with the concentration of stannous sulfate in the solution obeys the same pattern at a current density of 10 A/dm². However, the concentration value of stannous sulfate beyond which the deposition of tin dominates at the current density of 10 A/dm² is greater than that at the current density of 3 A/dm² (Figure 7.3). This implies that
using their electrolyte formulation, it is possible to change the deposit cobalt content from zero to some higher values by changing the applied current density only.

With reference to this study, a sulfate/gluconate bath was made up to obtain the desired curves of deposit composition vs. current density. Since the maximum cobalt content in deposits was expected to be 20 wt.%, the content of cobalt in the solution was set to this value. This is reasonable because the codeposition of tin and cobalt from the sulfate/gluconate solution was mainly reported as a normal system [37, 44]. The more noble metal, tin, was deposited preferentially. The content of the less noble cobalt was not more than its metal percentage in the solution. However, it was found from electroplating trials that the deposits obtained at all current densities under the electroplating conditions specified by Rehim et al. [44] were dark and powdery. Their results were not able to be repeated. Consequently, some further modifications were made. The electroplating temperature was raised from 25°C, as used in the reference, to 45°C, and some addition agents, gelatine and/or Tween 20, were added to the electrolyte. This leads to a new sulfate/gluconate electrolyte (as given in Table 6.2) for the deposition of acceptable Sn-Co alloys.

7.1.2.1 Deposit composition-current density relationship

The relationship between the deposit composition and the applied current density obtained from the new sulfate/gluconate electrolyte is shown in Figure 7.4. When the current density was lower than 0.3 A/dm², no cobalt was detected in the deposit using EDX analysis. The deposit seemed to be comprised of tin alone. Further increase in the current density led to a sharp increase in the cobalt content in deposits to a peak value of about 20 wt.%, followed by a gradual decline. This deposit composition-current density relationship is very close to the desired one for CMA production as illustrated in Figure 6.1, except that the applicable current density for the deposition of pure tin is no more than 0.3 A/dm². This means a relatively long electroplating time has to be spent on the deposition of soft tin layers, which is a disadvantage from an industrial production viewpoint.

7.1.2.2 Appearance and morphology

From Figure 7.5 it can be seen that at the current densities of 0.3 A/dm² and 0.5 A/dm², the dendrites dominate on the surface of the deposits. As a result, these deposits appear dark and loose. For deposits obtained in the current density range of 1-3 A/dm², the surface
becomes smooth and only some nodular grains can be seen on the surface. Correspondingly, the deposit obtained at 3 A/dm² looks lustrous. When the current density was increased to 5 A/dm², the edge of the sample became burnt, while the centre became dull again with the presence of more nodules.

As can be seen from sections 7.2.1 and 7.2.2, this new electrolyte formulation was very promising due to the fact that it allowed two desirable current density ranges to be defined. Further work on this new electrolyte was thus undertaken and aimed to

- Widen the current density range for deposits of pure tin, while maintaining the quality of deposits at higher current densities. This was thought to be achievable by shifting to the higher current density end the whole curve of deposit composition vs. current density. Therefore a series of experiments were carried out to decide how the variation of the physical and chemical parameters of the electrolyte affect the deposit composition-current density relationship.
- Remove dendrites from the deposit within the lower current density range. For this scenario, additives were considered.

### 7.1.2.3 Effect of variables of bath composition

(1) Solution cobalt content

In order to widen the workable current density range for the deposition of pure tin deposits, the cobalt content (or the ratio of tin to cobalt ions) in the solution was varied at first. Keeping the total metal molarity the same as that in the basic bath in Table 6.2, i.e. approximately 0.085 mol/l, the cobalt content in the solution was varied from 10% to 37%. The corresponding concentration of metal salts is listed in Table 7.3.

As shown in Figure 7.6, the composition of the deposits from the different solutions containing more than 17wt.% cobalt, varies similarly with increase in the applied current density. The maximum cobalt content in the deposit from each solution, which is close to the cobalt content in the solution, was obtained within the current density range of 1-2 A/dm². With increase in the cobalt content in the solution, the cobalt content in the deposits increases, however, the current density range for the deposition of pure tin deposits is hardly affected. On the other hand, the cobalt content in the solution could not be decreased below 10%, since at this concentration in the solution the cobalt content in the deposit decreased consistently with increasing the current density from 0.5 A/dm². As a
result, no desired compositional modulation could be achieved. Therefore, the cobalt content in the solution is important in deciding the maximum cobalt content in Sn-Co alloy deposits, but it can't be employed to widen the current density range for the deposition of pure tin deposits.

<table>
<thead>
<tr>
<th>Cobalt content in the solution wt.%</th>
<th>Concentration of stannous sulfate g/l</th>
<th>Concentration of cobalt sulfate g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>15</td>
<td>4.5</td>
</tr>
<tr>
<td>17</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>20</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>25</td>
<td>11</td>
<td>9.5</td>
</tr>
<tr>
<td>33</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>37</td>
<td>8.5</td>
<td>13</td>
</tr>
</tbody>
</table>

(2) pH value of the solution
The pH value of the new sulfate-gluconate electrolyte plays an important role in not only the cobalt codeposition but also the chemical stability of the solution. First, only at around pH 4.0 is the desirable curve of deposit composition vs. current density available (Figure 7.7). At pH 1-2, the deposition of cobalt at all of the current densities was totally inhibited (not plotted in the Figure 7.7). The composition analysis indicated no or little cobalt in the deposits. At pH 5-6, the cobalt content in the deposits declined with increasing current density consecutively. Conversely, when the pH value of the solution was adjusted to 8 or 9, the cobalt content in the deposits increased slowly with increasing current density and was much lower than the 20% cobalt content in the solution.

Secondly, the alkaline sulfate-gluconate baths with a pH value higher than 8 were quite unstable. A large quantity of a pinkish precipitate occurred in the solution after a period of time electroplating at 45°C. The solution, after filtration, looked white rather than dark pink before the precipitation took place. Compositional analysis of these precipitates by
CHAPTER 7 RESULTS AND DISCUSSION

EDX shows that they were rich in cobalt. The percentage weight ratio of cobalt to tin in the precipitates was 0.42 compared to 0.27 in the solution. These precipitates could be completely redissolved by adjusting the pH value of the solution to about 1.7. However, precipitation did not return when the regenerated solution was readjusted to even higher pH values.

(3) Total metal concentration of the bath

Keeping the ratio of tin to cobalt in the solution constant, the total metal (tin and cobalt) concentration of the bath was changed by simply diluting or concentrating the standard electrolyte in Table 6.2. The concentrations of stannous sulfate, cobalt sulfate, and sodium gluconate in the diluted or concentrated solutions are given in Table 7.4. Other parameters of the electroplating process remained unchanged as that in Table 6.2. The corresponding effect of the total metal concentration of the bath on the deposition of tin-cobalt alloys is shown in Figure 7.8.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Half diluted</th>
<th>Standard</th>
<th>Double concentrated</th>
<th>Three-fold concentrated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannous sulfate</td>
<td>6</td>
<td>12</td>
<td>24</td>
<td>36</td>
</tr>
<tr>
<td>Cobalt sulfate</td>
<td>4</td>
<td>8</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>30</td>
<td>60</td>
<td>120</td>
<td>180</td>
</tr>
</tbody>
</table>

Inspection of Figure 7.8 reveals that diluting the standard solution shifts the whole composition curve to lower current density end, while concentrating the standard solution shifts the whole curve in the opposite direction. Consequently, the more concentrated the solution, the wider the current density range suitable for electroplating deposits of pure tin.

Although from the view-point of deposit composition-current density relationship, concentrating the solution is favourable, the appearance of the deposits from the three-fold concentrated solutions is only acceptable at the current density of around 1 A/dm². In these circumstances, some appropriate addition agents need to be added to the solution.
formulation in order to improve the surface quality of the higher cobalt content deposit obtained at higher current densities.

(4) Concentration of complexing agent
The concentration of sodium gluconate, which forms complex ions with both tin and cobalt, was varied from 20 to 80 g/l so that the molar ratio of the complexing agent to tin and cobalt in the solution was altered from 1:1 to 1:4. As can be seen from Figure 7.9, the variation in sodium gluconate concentration from 40 to 80g/l does not show conclusive influence on the deposition of Sn-Co alloys. The cobalt contents in the deposits obtained at the same current density only fluctuate slightly with the variations in the concentration of sodium gluconate. For the solution containing 20g/l sodium gluconate, however, the cobalt in the deposits does not show a peak value but keeps on decreasing with increase in the current density. This suggests that the molar ratio of the complexing agent to the sum of tin and cobalt ions in the solution should not be smaller than 1:1, otherwise, the desired deposit composition-current density relationship could not be maintained. Too high a ratio, on the other hand, increases the cost. Therefore the optimum concentration of sodium gluconate should be two or three times the total molar concentration of tin and cobalt ions in the solution.

(5) Concentration of supporting electrolyte
Sodium sulfate was added to the electrolyte for the purpose of increasing conductivity. It was not expected to show a marked influence on the cobalt content in the deposits. However, in practice, the concentration of sodium sulfate changes the cobalt content in the deposits greatly (shown in Figure 7.10). The optimum concentration of sodium sulfate seems to be 20g/l.

7.1.2.4 Effect of electroplating conditions
(1) Agitation strength
Figure 7.11 shows the influence of agitation strength on the cobalt codeposition in the typical sulfate-gluconate bath. The agitation strength increases in the order of no agitation, mild (Mark 6), moderate (Mark 8), and vigorous agitation (Mark 9). (Mark 6, 8, and 9 are the marks on the hot plate to indicate the rotating speed of the magnetic stirrer). It is obvious that cobalt codeposition is very sensitive to the agitation strength. The whole curve of the cobalt content vs. current density shifts to the right with increase of agitation
strength. This broadens the current density range for the deposition of low cobalt content Sn-Co alloys. Therefore, the application of appropriate agitation is a possible way to speed up the deposition of low cobalt alloys. However, in practice, the uniformity of agitation and consequently the process reproducibility becomes a major concern and problem when agitation is employed.

The deposit obtained within the lower current density range was still dark and loose, even with strong agitation. Once again, this problem called for the addition of appropriate additives. Within the higher current density range, the deposit obtained with agitation was visually acceptable, but not uniform. The deposit at the upper stream of the moving solution on the cathode surface was semi-bright, while the deposit at the down stream was dark and not satisfactory.

In view of the remarkable effects of both the total metal concentration of the solution and the application of agitation on the deposition of Sn-Co alloy coatings, it was expected that there exists a synergistic effect of agitation and the concentration of the solution. To confirm this presumption, different levels of agitation by magnetic stirring were applied in the three-fold concentrated solution (see Table 7.4). Its effect on the cobalt content in the deposit is presented in Figure 7.12. With comparison to Figure 7.11, agitation in the concentrated solution produces a much greater effect on the deposition characteristics than the individual effects of either agitation or variation of the solution concentration alone. In the standard solution, vigorous agitation expands the current density range for pure tin deposition up to 2 A/dm². However, in the three-fold concentrated solution, even moderate agitation enables the deposition of pure tin at the current density of 3 A/dm². When vigorous agitation is applied, this current density threshold is as high as 6 A/dm². Beyond this current density, the codeposition of cobalt takes place, but the cobalt content in the deposit is very low. The cobalt content in deposit obtained at the applied current density of 8 A/dm² is only about 3%. This strong synergistic effect suggests the necessity of a proper control over the agitation level during the deposition of Sn-Co alloys from a sulfate/gluconate bath in order to obtain reproducible results.

(2) Temperature of the solution
The effect of temperature on the cobalt content in the deposits seems different within different current density ranges (Figure 7.13). When the current density is less than
1A/dm$^2$, increasing temperature decreases the cobalt content. Conversely, when the current density is larger than 1A/dm$^2$, increasing temperature tends to increase the cobalt content in the deposit.

Although increasing the operating temperature did not significantly affect the problem of the current density ranges, the surface quality of the deposit obtained at higher electroplating temperature was more satisfactory. Therefore following these investigations, further trials were always carried out within the temperature range of 45-50°C, taking into consideration also the accelerated oxidation of tin(II) ions in the solution at elevated temperatures.

### 7.1.3 Hull cell tests

As revealed in section 7.1.2, the deposit composition-current density relationship obtained in the new sulfate/gluconate electrolyte was desirable. However, for all those experiments, satisfactory deposits were only produced at the current density range of 1-3A/dm$^2$. Deposits obtained at current densities lower than 1A/dm$^2$ were black and dendritic. It was impossible to produce multilayer coatings under those conditions. Considering the deposition of tin dominates at low current densities and the electrolyte used is acidic, the formation of loose deposits must arise from the preferential growth of tin crystals at points or edges on the cathode, which is a common observation in the deposition of tin from acidic solutions without additives [50]. The general solution to this problem is to add some suitable organic additives to increase the polarisation on tin deposition and thus inhibit its preferential growth into dendrites.

In the previous experiments (Section 7.1.2), 0.5g/l gelatine was added to the solution. Hence the effect of the quantity of gelatine was studied first using Hull cell tests, followed by the investigation of the effect of additions of a non-ionic surfactant-Tween 20- alone or with gelatine. Figure 7.14 shows the effect of gelatine. From the low current density end to the high current density end of the test panel, there are mainly three zones, within which the deposit appeared dark grey, bright, and burnt, respectively. By appearance, only the deposit in the bright zone is acceptable. With addition of gelatine at less than 1g/l, there was no bright zone on the surface of the test panel. The bright zone only appeared when
the quantity of gelatine in the solution was greater than 2 g/l. However, this zone became narrower and shifted to the lower current density end of the panel with further increase in the quantity of gelatine, suggesting an overdosing effect. It is obvious that gelatine is only effective within a narrow current density range and the optimum concentration is around 2 g/l. Addition of gelatine alone is not adequate for the purpose of multilayer coatings because no acceptable tin deposits could be produced at lower current densities.

Figure 7.15 illustrates the effect of Tween 20 on the deposition of tin-cobalt alloy. Unlike gelatine, the addition of 3-4 ml/l Tween 20 allowed satisfactory deposits to be produced at two current density ranges. One was at the low current density end (less than 0.4 A/dm²), the other was within the medium current density range from about 1 to 1.5 A/dm². Although both current density ranges were relatively narrow, they did demonstrate the possibility of deposition of tin and tin-cobalt alloys from a single bath by varying the current density only. Therefore, addition of Tween 20 was promising.

Figure 7.16 shows the effect of the addition of different quantities of Tween 20 to the solution in which 2 g/l gelatine had already been added in advance. In comparison to Figures 7.14 and 7.15, it can be seen from Figure 7.16 that at the lower current densities, Tween 20 in the presence of gelatine was as effective as when it was added alone. However, at medium current densities, Tween 20 simply stopped gelatine from functioning. Within the current density range where gelatine alone was effective, the deposit either looked dark grey, or silver grey with many dark streaks. These streaks were found, under SEM inspection, to be due to the formation of dendrites. Therefore there is no indication that Tween 20 and gelatine complement each other. It is Tween 20 that shows the predominant effect on the deposition of tin and tin-cobalt alloys when it is added together with gelatine.

As indicated by the results from Hull cell tests, there might exist some organic addition agents which are more effective than Tween 20 and enable the successful deposition of tin and tin-cobalt alloys within two wide and separated current density ranges. However, identifying such agents is usually achieved by a trial-and-error method. In view of the large quantity of organic agents, it is envisaged that this process would be very difficult. Under these circumstances, pulse electroplating, which has been established as an effective technique of modifying the electrocrystallisation of deposits [68], has been suggested as
another option to overcome the formation of dendrites during the deposition of tin-cobalt alloys.

7.2 Electrodeposition of tin-cobalt alloys Part II Pulse electroplating

7.2.1 Pulse electroplating trial

7.2.1.1 Deposit appearance

Trial experiments were carried out using the electrolyte given in Table 6.3 to verify whether it was feasible to overcome the formation of dendrites during the deposition of tin-cobalt alloys by using pulsed current. Figure 7.17 shows the effect of three different current waveforms on the appearance of Sn-Co alloy deposits. It can be seen that under pulsed current conditions, a great improvement was achieved in the appearance of deposits obtained at higher peak/average current densities (see Figure 7.16 for the deposit appearance under direct current conditions). For different off-times, there always exists a peak current density range within which dendrite formation was totally inhibited and as a result, bright and smooth deposits were obtained. The thickness of the bright deposits was about 10 microns. With increase in the off-time from 4ms to 19ms, the corresponding peak current density range for bright deposits becomes wider and shifts to higher values. However, the corresponding average current density range for bright deposits showed a different tendency in relation to the variation of the off-time (Figure 7.17 (b)). For the waveforms with longer off-times and therefore higher peak current densities, the average current density range for bright deposits becomes narrower and shifts to the lower current density end. In other words, the useful average current density window is wider for waveforms with higher duty cycles.

7.2.1.2 Deposit composition and current efficiency

The effect of different current waveforms on the cobalt content of deposits is given in Figure 7.18. The cobalt content of the deposits for each electroplating condition increases with peak current density and then levels off at a value which is close to the cobalt concentration in the solution. The whole curve shifts towards the higher peak current density end with increase in the off-time. At the same peak current density, the deposition of cobalt is less favoured under pulse conditions with longer off-times. As with the
observations for deposit appearance (Figure 7.17), when the deposit composition is plotted against the average current density, although the cobalt content still increases with average current density, the whole curve shifts towards the lower average current density end. At the same average current density, the deposition of cobalt is favoured with increasing off-time.

As shown in Figure 7.19, the current efficiency decreases with increase in the peak or average current density almost linearly. At the same peak current density, the current efficiency increases with increase in the off-time. On the contrary, at the same average current density, deposition with a shorter off-time shows higher current efficiency. On this basis, the codeposition of cobalt with tin and the evolution of hydrogen vary in the same way with the variations in peak or average current densities.

### 7.2.2 Hull cell tests

Following the successful pulse electroplating trial, a systematic study was conducted in order to clarify the effect of various electroplating parameters on the deposition of tin-cobalt alloys. Hull cell tests were employed to investigate (1) the effect of pulsed current parameters, (2) the effect of Tween 20, and (3) the critical cobalt content in the solution below which even pulsed current could not prevent the dendritic growth of tin-cobalt alloy electrodeposits.

The electrolyte used in these tests is given in Table 6.4. The difference between electrolytes in Table 6.3 and Table 6.4 is that in the latter (1) 30 g/l boric acid was added as a buffering agent to stabilise the pH value of the bulk electrolyte, (2) the temperature of the solution was maintained within the range of 45–50°C, and (3) there was no addition of gelatine. The reason for not using gelatine is that addition of Tween 20 alone was found to produce better results in the presence of boric acid. It is worth noting that the addition of boric acid was later found to be very important as it made the deposition of satisfactory tin-cobalt alloys at higher current densities become much easier (See Figure 7.20).
7.2.2.1 Effect of duty cycle

The duty cycle of the applied current waveform was varied from 100% (direct current) to 10%. Its effect on the Hull cell behaviour is shown in Figure 7.20. There are mainly four zones on the test panels from right to left (or from the low current density end to the high current end). The deposit looked off-white in zone I, dark grey in zone II, silver grey in zone III, and finally burnt in zone IV. The morphologies of deposits from different zones are given in Figure 7.21. In zone I, the deposit showed an angular crystal morphology. In zone II, the deposit becomes porous with more discrete crystals distinguishable. In zone III, the deposit was nodular and compact, whilst the nodule size increased as the current density increased. The visually acceptable zones are zone I at the low average current density end, and zone III covering a wide medium current density range. Compositional analysis indicated that the deposit in zone I was mainly tin, while the cobalt content of deposits in zone III was approximately 12-14 wt.%. As can be seen from Figure 7.20, under direct current electroplating conditions, zone I extends up to the current density of around 0.5 A/dm². Zone III covers the current density range from 1.5 to 5 A/dm² approximately. With the application of pulsed current, zone I becomes more and more narrow with decrease in duty cycle from 90% to 10% (the corresponding peak current flowing through the test cell varies from about 1.1A to 10A). Zone III expands in two directions, mainly towards the low current density end. The width of zone III increases with decrease in duty cycle down to about 33%. Further decrease in duty cycle, on the contrary, makes zone III become narrower, leaving deposits in a wider zone IV being burnt. Consequently, an optimum pulsed current waveform exists in terms of the current density range for the deposition of satisfactory tin-cobalt alloy deposits.

However, the application of pulsed current has some disadvantageous effects with respect to the deposition of the desired multilayer coatings. It shifts the current density range for the deposition of pure tin deposits to the lower current density end, and thereby decreases the maximum deposition rate available for pure tin deposits. Therefore, for a successful electrodeposition of compositionally modulated tin-cobalt alloy multilayer coatings, pulsed current should be used for the deposition of hard layers of tin-cobalt alloys, but direct current should be used for the deposition of soft layers of pure tin.
7.2.2.2 Frequency
Apart from the duty cycle, another important parameter of a pulsed current is its frequency. Figure 7.22 illustrates the effect of the frequency of the pulsed current on the deposition of tin-cobalt alloys. For all the duty cycles, frequency has negligible effect on zone I, although it seems that zone I becomes slightly narrower with decrease in frequency. As to zone III, for waveforms with high duty cycles, i.e., 90% and 80%, its width increases slightly with decreasing frequency. The major difference brought about by the decrease of frequency is that the higher current density end of zone III adjacent to zone IV becomes darker and rougher, which suggests higher tendency towards powdery deposition.

For waveforms with duty cycles of 50% and 33% (Figure 7.22 (c) and (d)), the width of zone III increases with decrease in frequency. However, decreasing the frequency down to a certain value, i.e. 5Hz for the duty cycle of 50% and 166Hz for the duty cycle of 33%, introduces a new zone between Zone III and IV. In this new zone, the deposit was either completely bright (at higher frequencies), or mainly bright with grey streaks (at lower frequencies).

For waveforms with a duty cycle of 20% or 10%, decreasing the frequency was found to be disadvantageous. When the frequency is lower than 10Hz for 20% duty cycle, or 50Hz for 10% duty cycle, zone III splits into two sections. The section at the higher current density end tends to be dark and more burnt-like. The section at the lower current density end is still silver grey. Due to the formation of dark deposits, the current density range for acceptable tin-cobalt alloy deposits becomes narrower with decrease in the frequency.

In summary, variation in the frequency does not have noticeable influence on the width of zone I where the deposition of tin dominates. The effect of frequency on the width of zone III where cobalt codeposits with tin is related to the duty cycle of the applied current waveform. Normally, zone III expands towards the lower current density end and becomes wider with decrease of the frequency. However, at low duty cycles such as 10%, the deposits at higher current density end of the test panel are more likely to be burnt when the frequency is low, and as a result, Zone III becomes narrower. On this basis, at lower duty cycles, higher frequency is always desirable.
7.2.2.3 Effect of Tween 20

Figure 7.23 shows the effect of the quantity of Tween 20 on tin-cobalt alloy deposition in the electrolyte with 30 g/l boric acid. Without addition of Tween 20, the whole test panel was almost black and powdery. However, even though only 1 ml/l Tween 20 was added, silver grey tin-cobalt alloy could be obtained within a wide current density range of approximately 1.5-4 A/dm$^2$ (Zone III in Figure 7.23). With further increase in the quantity of Tween 20, the width of this current density range increases continuously. In addition, the quantity of Tween 20 doesn’t show an apparent effect on the width of zone I, where off-white deposits were always observed.

7.2.2.4 Critical cobalt content in electrolyte

Although for a preliminary study on the properties of tin-cobalt alloy multilayer coatings, around 20% cobalt in the hard sublayers had been suggested, the composition configuration of the multilayer coatings was also expected to be varied and thus optimised in a series of experiments. One of the most likely approaches to accomplish this optimisation is varying the cobalt content in the electrolyte (see Figure 7.6). Therefore some work was carried out to reveal the electrochemical behaviour of the electrolytes containing different contents of cobalt.

The cobalt content in the test solution was varied from 12% to 40% while the total molar concentration of tin and cobalt salt, and the quantity of other chemicals remained constant. Table 7.5 gives the quantity of cobalt and stannous sulfate in each electrolyte. The results of Hull cell tests on each solution is presented in Figure 7.24. Obviously, as a result of decreasing cobalt concentration and increasing tin concentration in the solution, although the current density range for pure tin deposits is marginally wider, the current density range for harder Sn-Co alloy deposits became more and more narrow. In the end, there is a critical cobalt concentration in the electrolyte, below which no acceptable deposit could be produced at higher current densities. This critical cobalt content is between approximately 12% and 15%. However, it is necessary to emphasise that this critical cobalt concentration only holds for the specified total molar concentration of metal ions (0.25M) and 120g/l sodium gluconate.
### Table 7.5 Electrolyte formulations of different cobalt concentration

<table>
<thead>
<tr>
<th>Cobalt content in solution</th>
<th>Tin(II) sulfate</th>
<th>Cobalt sulfate</th>
<th>Total molar concentration of tin and cobalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>g/l</td>
<td>g/l</td>
<td>M</td>
</tr>
<tr>
<td>12</td>
<td>43</td>
<td>15</td>
<td>0.25</td>
</tr>
<tr>
<td>15</td>
<td>41</td>
<td>19</td>
<td>0.25</td>
</tr>
<tr>
<td>20</td>
<td>36</td>
<td>24</td>
<td>0.25</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>33</td>
<td>0.25</td>
</tr>
<tr>
<td>40</td>
<td>23</td>
<td>41</td>
<td>0.25</td>
</tr>
</tbody>
</table>

#### 7.2.3 Characterisation of deposit composition

**7.2.3.1 Effect of frequency**

The frequency of the waveforms with different duty cycles was varied from the highest value available with the pulse electroplating unit to an order of magnitude of several hertz. Its effect on the composition of the deposit is shown in Figure 7.25. For the waveform with a high duty cycle of 80% (Figure 7.25(a)), the cobalt content in the deposits obtained at the same average current density of 1 A/dm² decreases with increase in frequency. However, this effect becomes less significant with increasing average current density. The cobalt content in the deposit is actually almost constant for all the frequencies when the average current density is 3 or 4 A/dm².

When the duty cycle of the current waveform was decreased to 50% (Figure 7.25(b)), the same tendency of the frequency effect is observed except that the curve for the average current density of 1 A/dm² shifts to higher cobalt contents. As a result, these curves become closer and the difference in the cobalt content between different average current densities diminishes.

However, at a duty cycle of 20%, it was found that the frequency does not affect the deposit composition anymore (as shown in Figure 7.25(c)). Meanwhile the cobalt content...
in the deposits within the average current density range of 1-4 A/dm² tends to be similar, which is close to the cobalt concentration in the solution.

In general, the effect of frequency of the pulsed current waveform on the deposit composition has dependence on both the duty cycle and the applied average current density. At average current densities greater than 2A/dm², the frequency shows insignificant effect on the deposit composition for all duty cycles. At the average current density of 1 A/dm², with increase in frequency, the cobalt content in the deposit either decreases for current waveforms of duty cycles higher than 50%, or remains a constant for current waveforms of small duty cycles, i.e. lower than 20%.

7.2.3.2 **Effect of on-time**

Figure 7.26 shows the effect of on-time of pulsed current waveforms with fixed off-time of 1millisecond and 10 milliseconds, respectively. For comparison the composition of the deposits obtained with direct current is also plotted. Apparently, the whole curve of the deposit composition against the peak current density shifts towards the left with increasing on-time. As a result, the cobalt content in deposits obtained at the same peak current density and off-time increases when the corresponding on-time is lengthened.

With comparison to direct current electroplating, it can also be seen that at the constant off-time of 1millisecond, the composition curve under pulsed current conditions approaches that using direct current, with increase in the on-time (and correspondingly an increase in the duty cycle). When the on-time is long enough, e.g. 4 and 9 milliseconds, the curves for the pulsed currents and direct current tend to merge together, although some differences do exist at higher current densities. As this difference is not significant, it cannot be concluded whether it is due to the effect of the on-time or experimental error. In this circumstance, it is interesting to wonder if with increase in the on-time, which leads to a condition more close to direct current electroplating, the curves under pulsed current conditions in Figure 7.26(a) could shift beyond, or to the left side of the direct current one. The answer to this question was found when the off-time was longer.

As shown in Figure 7.26(b) at longer constant off-time of 10 milliseconds, a similar dependence of deposit composition on the on-time was observed, i.e. the longer the on-time, the higher the cobalt content of the deposit is at the same peak current density.
Meanwhile Figure 7.26(b) definitely shows that the curves with an on-time longer than 40ms are on the left side of the curve for direct current. As a result, the cobalt content in deposits obtained under these pulsed current conditions is even higher than the corresponding value obtained with direct current at the same peak current densities.

On the other hand, when the deposit composition was plotted against average current density (Figure 7.27), it was found that the cobalt content in the deposit under pulsed current conditions seems always higher than that using direct current, particularly when the average current density is not more than 2 A/dm². The variation in the deposit composition with on-time is mainly distinguishable around 1 A/dm². Within this average current density range, the increase in the on-time of the waveform with constant off-time leads to a decrease in the cobalt content in the deposits. At the same average current densities higher than 2-3 A/dm², the difference in the deposit composition at varying on-times diminishes.

7.2.3.3 Effect of off-time
Keeping the on-time at a constant value of 1 millisecond and 10 milliseconds, respectively, the effect of the off-time was studied. From Figure 7.28, it can be seen that with an increase in the off-time, the family of curves moves to the right with increasing off-time. As a consequence, the cobalt content at the same peak current density decreases with increase in the off-time.

Just like the effect of on-time, when the deposit composition is plotted against the average current density (Figure 7.29), All these curves shift in the opposite direction, i.e. towards the left with increasing off-time. Meanwhile the noticeable difference in the deposit composition due to the variation in the off-time is only observed at the average current density of around 1 A/dm², with higher cobalt content at longer off-times.

7.2.3.4 Effect of peak and average current density
The effect of peak and average current density can be seen from Figures 7.26 to 7.29. It is evident that, irrespective of what type of pulsed current waveforms is applied, the cobalt content in deposits always increases with increasing peak or average current density under comparable conditions. The rate of increase in the deposit cobalt content, however, slows down at higher peak or average current densities. Consequently the cobalt content finally comes to a plateau value and the applied current density does not have effect. This implies
that under these current densities the deposition is completely controlled by the mass transport process. Further increasing the applied current density only leads to a decrease of cathodic current efficiency due to hydrogen evolution and the formation of burnt deposits.

7.2.4 Current efficiency in pulse electroplating

As far as the cathodic current efficiency is concerned, it can be seen from Figure 7.30 that the effect of frequency of the pulsed current waveform with any duty cycle from 10% to 90% is negligible. The current efficiency is mainly a function of the applied current density and the duty cycle. With increase in the average (or peak) current density the current efficiency decreases continuously, which is usually observed in electroplating systems. However, no such simple relationship was found between the variation of the current efficiency with the duty cycle. Figure 7.31 illustrates the effect of the duty cycle on the deposition efficiency. The current efficiency at each data point is an average value of those obtained with various frequencies. As a general trend, with decreasing the duty cycle from 100%, the efficiency increases initially and reaches a maximum value at a 67% duty cycle. Further decrease in the duty cycle leads to a gradual decrease of the current efficiency. In comparison, the current efficiency under the pulsed current conditions could be higher or lower than that under the direct current condition at the same average current density. At the same peak current density, however, the current efficiency is always higher for pulsed current than direct current.

7.2.5 Addition of Tween 20

7.2.5.1 Concentration effect

As indicated by the result of the Hull cell tests (see section 7.2.2.3), Tween 20 plays an important role in the deposition of satisfactory tin-cobalt alloys from the modified sulfate/gluconate bath. Adherent tin-cobalt alloy coatings were only produced with the addition of Tween 20. The quantity of Tween 20 in the solution also shows some effect on the appearance of the deposit. Based on this qualitative information, further experimentation was subsequently performed to quantify the effect of Tween 20 on the cobalt content of the deposit and the corresponding current efficiency.
Figures 7.32 and 7.33 give the results obtained at two current densities, i.e. 0.5 A/dm$^2$ and 3 A/dm$^2$. At 0.5 A/dm$^2$ the coating was deposited using direct current. At the average current density of 3 A/dm$^2$ a pulsed current with a duty cycle of 50% and a frequency of 500Hz was applied. The electrolyte used contained 15% and 20% cobalt, respectively. It can be seen that tin is the main component of the deposit and no noticeable influence of Tween 20 is observed at the current density of 0.5 A/dm$^2$. However, at 3 A/dm$^2$, with increasing the concentration of Tween 20 there is an apparent initial increase in the cobalt content of the deposits. The effect of Tween 20 then levels off at higher concentrations. The cobalt content in deposits only shows a slight increase within the concentration range of Tween 20 from 6ml/l to 14ml/l. As far as the current efficiency is concerned, addition of Tween 20 shows little influence. Only a slight decrease in the cathodic current efficiencies at both current densities was observed even though the concentration of Tween 20 was increased from 2 to 14 ml/l.

Therefore from the viewpoint of the stability of the deposit composition and the process reproducibility, higher concentration of Tween 20 is favourable in case decomposition of Tween 20 takes place during the electrodeposition. However, as can be seen later, a high concentration of Tween 20 has some adverse effect in terms of deposit properties such as the internal stress.

7.2.5.2 Cloud point temperature

During the research, it was noticed that the solution with the addition of Tween 20 sometimes became cloudy at higher temperature than about 40-50°C, depending on the composition or even the preparation process of the electrolyte, and the solution became clear again after the temperature was lowered. This feature imposes some limits on the workable temperature range of the electrolyte. Therefore some consideration was given to this physical phenomenon, so as to provide a guide on optimisation of the electroplating bath. It was later found that this phenomenon was caused by the addition of Tween 20.

Tween 20, also known generically as Polysorbate 20 or Polyoxyethylene-20-sorbitan monolaurate, is a non-ionic surfactant. Non-ionic surfactants dissolve in water by the hydration of ether oxygens of the polyoxyethylene group. This kind of link is weak. An increase in temperature causes the cleavage of the hydrogen bond between the ether oxygen and the hydrated hydrogen. As a result, the solubility of the non-ionic surfactant decreases
and the solution becomes a cloudy dispersion. The temperature above which the non-ionic surfactant solution becomes cloudy is termed as the 'cloud point'. Above the cloud point the non-ionic surfactant ceases to perform some or all of its normal functions as a surfactant. The cloudy solution will normally become clear again after it is cooled down below this temperature threshold. This is exactly what has been observed in the present investigations.

To some extents, the cloud point is usually influenced by the presence of other chemicals in the solution. Therefore some measurements were carried out to study the effect of all the chemical components of the new sulfate/gluconate electrolyte on the cloud point temperature of Tween 20.

As shown in Table 7.6, the cloud point temperature is obviously not affected by the amount of Tween 20 itself in deionised water. It remained a constant of 88°C. With addition of other chemicals, however, the cloud point temperature either increases or decreases. In Table 7.7, with increasing the concentration of sodium gluconate in deionised water, the cloud point temperature drops markedly from 80°C to 33°C whilst the pH value of the solution increases slightly. Another component of the electrolyte which has a remarkable effect on the cloud point temperature is the conductive salt, i.e. the sodium sulfate (Table 7.8). Addition of cobalt sulfate decreases the cloud point temperature, but the concentration of cobalt sulfate does not show a strong effect (Table 7.9). Table 7.10 gives the effect of the addition of boric acid alone on the cloud temperature. Apparently, boric acid has the least influence and the cloud point temperature is nearly the same as that of the solution with Tween 20 only.

<table>
<thead>
<tr>
<th>Tween 20 ml/l</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>6.4</td>
<td>6.27</td>
<td>6.17</td>
<td>5.98</td>
</tr>
<tr>
<td>Cloud point °C</td>
<td>88</td>
<td>87</td>
<td>88</td>
<td>88</td>
</tr>
</tbody>
</table>
To study the effect of tin sulfate, hydrolysis of tin(II) must be inhibited. When tin sulfate was dissolved in water alone, the solution after filtration was cloudy because of the hydrolysis of tin(II) ions. Although the cloudy solution could become clear after the pH value of the solution was adjusted below 1, the solution became pale yellow and cloudy again after standing for more than one day. Therefore the complexing agent, sodium gluconate, was added first to stop the hydrolysis of tin(II). The results in Table 7.11
indicate that tin sulfate in the solution containing 120g/l sodium gluconate has only a small effect on the cloud point temperature. The cloud point temperature remains near 62°C, which is the value for the solution with 120g/l sodium gluconate alone.

Table 7.12 gives the cloud point temperature of the electrolyte with all components present, but various concentrations of cobalt. It can be seen that with variations in the cobalt metal content, the cloud point temperature was always within the range of 50-52°C. This further proves that the concentrations of stannous sulfate and cobalt sulfate do not have a great effect on the cloud point temperature of the electrolyte. However, it is worthy to note that the cloud point temperature can be decreased by inadequate filtration to remove the insoluble tin species during the solution preparation. The decrease becomes more severe when the cobalt content in the solution is low and therefore the concentration of stannous sulfate is high. It was once found that the cloud point temperature for a 5 litre solution containing 15% cobalt was only 42°C. After it was refiltered, the cloud point temperature rose to about 52°C again.

<table>
<thead>
<tr>
<th>Table 7.11 Effect of stannous sulfate on the cloud point temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSO₄ g/l</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Cloud point °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 7.12 Cloud point temperature for the solution with varying cobalt contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt content wt.%</td>
</tr>
<tr>
<td>Cloud point °C</td>
</tr>
</tbody>
</table>

To make the cloud point temperature of the electrolyte well above the desired working temperature range of 45-50°C, further modification of the electrolyte was considered. Taking into consideration its effect and large quantity which has to be added into the solution, sodium gluconate was in practice the main factor in determining the cloud point temperature in comparison to the other chemical components. Therefore one of the most
likely approaches to increase the cloud point temperature was to decrease the concentration of sodium gluconate. However, as sodium gluconate is a complexing agent, its concentration in the solution affects the stability of the complexes of tin and cobalt, as well as their codeposition. The concentration of sodium gluconate could not be less than a certain minimum value. A compromise thus needed to be made between the cloud point temperature and the deposit quality.

Table 7.13 reveals the variations of cloud point temperature and the deposit appearance with different quantities of sodium gluconate in solutions containing 35g/l tin sulfate, 16g/l cobalt sulfate, 30g/l boric acid, and 20g/l sodium sulfate. It can be seen that the lower the concentration of sodium gluconate, the higher the cloud point temperature. Nevertheless, the concentration of sodium gluconate should not be less than 90 g/l. Otherwise, the deposits obtained at the low current density end had poor coverage and no satisfactory tin deposits could be produced at 0.5A/dm².

<table>
<thead>
<tr>
<th>Sodium gluconate g/l</th>
<th>70</th>
<th>90</th>
<th>110</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloud point °C</td>
<td>64</td>
<td>60</td>
<td>57</td>
<td>52</td>
</tr>
<tr>
<td>Appearance of deposits</td>
<td>0.5A/dm²</td>
<td>Black and powdery</td>
<td>Off-white</td>
<td>Off-white</td>
</tr>
<tr>
<td>DC 3A/ dm²</td>
<td>Bright</td>
<td>Bright</td>
<td>Dark</td>
<td>Dark</td>
</tr>
<tr>
<td>PC 1-2ms 3A/ dm²</td>
<td>Bright</td>
<td>Bright</td>
<td>Bright</td>
<td>Grey</td>
</tr>
</tbody>
</table>

On the other hand, no more than 130 g/l sodium gluconate should be added into the solution if the operating temperature is specified as 45~50°C. With respect to the deposit quality, using high concentrations of sodium gluconate also leads to another adverse effect. With increasing the concentration of sodium gluconate, the deposits obtained at the
average current density of 3A/dm², tended to become dark and rough, no matter whether the applied current was a direct or a pulsed one.

As far as the deposit composition and deposition efficiency are concerned, sodium gluconate inhibits the codeposition of cobalt with tin at the current density of 3 A/dm², and thus decreases the cobalt content in deposits. However, it does not affect the deposit composition at 0.5 A/dm² (Figure 7.34). The effect of sodium gluconate on the cathodic current efficiency is slight (see Figure 7.35).

7.3 Compositionally modulated tin-cobalt alloy multilayer coatings

7.3.1 Morphology

7.3.1.1 Multilayer coatings on copper substrate
A tin-cobalt alloy multilayer coating was prepared on copper substrate by alternate deposition of tin-cobalt alloy sublayers using pulsed current at an average current density of 3A/dm², and tin sublayers by direct current at 0.5A/dm². The surface layer was tin. The thickness of both sublayers was about 1μm and the overall thickness of the multilayer coating was approximately 12μm. The surface morphology of the multilayer coating obtained is illustrated in Figure 7.36 (a). It has characteristic fine angular crystals (about 1-2 μm in width) on top of coarse nodules (about 20 μm in diameter). This is quite different from the observations for single layer coatings. As shown in Figure 7.36 (b) and (c), on the surface of a single layer tin coating with similar thickness, only well-developed pyramidal crystals were observed, whilst on the surface of a single layer tin-cobalt alloy coating there were only cauliflower-like nodules. The multilayer coating probably exhibits a combined surface morphology of all its both sublayers.

Another striking feature of the surface morphology of the multilayer coating is that the grain size of the outermost tin sublayer is quite small compared with that of the single layer tin coating deposited at the same current density. Conversely, the size of the nodules is larger than that for the single layer tin-cobalt alloy deposit. This implies that there might exist strong thickness effects for multilayer coatings, which was investigated and reported in detail in the following sections.
CHAPTER 7 RESULTS AND DISCUSSION

7.3.1.2 Thickness effect of tin sublayers

The thickness of tin sublayers was varied from 0.5µm to 3µm whilst the thickness of the tin-cobalt alloy sublayers was maintained at a constant of 1µm. The surface morphology of the consequent multilayer coatings is shown in Figure 7.37. As can be seen, the grain size of the outermost tin sublayer is directly related to its own thickness. With increase in the thickness of tin sublayers the grain size increases. This tendency is further proved by the morphology of single layer tin deposits with varying thickness (Figure 7.38).

The pores observed in Figure 7.37 (a) might suggest that thin deposits of tin do not have sufficient coverage. However, no pore is observed on the surface of a single layer tin deposit which was electroplated on the copper substrate to the same thickness (Figure 7.38 (a)). Meanwhile, there are no pores observed on the surface of a multilayer coating with the thickness configuration of 0.5µm alloy layers and 0.5µm tin layers. Therefore the pores in Figure 7.37(a) might not be a characteristic. These pores might be caused by a local insufficient pre-treatment.

The multilayer coating with 3µm tin sublayers presents a rough surface of very coarse nodular grains (Figure 7.37 (d)), which is not observed on the multilayer coatings with thinner tin sublayers (Figure 7.37 (a)-(c)). As it can be seen later, the nodule size of tin-cobalt alloy does not exhibit noticeable change with increase in deposit thickness, therefore the coarsening of these nodules suggests that they are amplified during the subsequent deposition of tin sublayers. Further investigation of this required the examination of coating cross-sections to eliminate the effect of the surface roughness of the substrate and the characterisation of the throwing power of tin sublayers (See section 7.3.2).

7.3.1.3 Thickness effect of tin-cobalt alloy sublayers

The thickness effect of tin-cobalt alloy sublayers on the surface morphology of the multilayer coating is given in Figure 7.39. There is no discernible change of the multilayer surface morphology with increase in the thickness of tin-cobalt alloy sublayers. The grain size of the outermost layer of tin is mainly governed by its own thickness. There are also no signs indicating that the nodule size is influenced by the thickness of tin-cobalt alloy sublayers.
In Figure 7.40, the effect of the thickness of a single layer deposit of tin-cobalt alloy on its surface morphology is shown. It can be seen that the nodule size of a tin-cobalt alloy deposit does not change significantly, even though the thickness of the deposit is increased from 0.5\(\mu\)m to 13\(\mu\)m. In addition, the morphology of the thin alloy deposit indicates that there exists apparent preferential growth along certain crystal directions of the substrate (Figure 7.40 (a)). On the surface of the thickest alloy deposit, there exhibit some cracks due to the accumulation of internal tensile stresses (Figure 7.40 (d)).

### 7.3.1.4 Waveform effect

Without changing the thickness configuration and the overall thickness of the multilayer coatings, the applied current waveform for the deposition of tin-cobalt alloy sublayers was varied. The effect is shown in Figure 7.41. The general trend is that with decreasing the duty cycle, the multilayer coating obtained becomes more and more rough. This might be explained by the effect of waveform of the pulsed current on the morphology of single layer alloy deposits. It was observed that the alloy deposit obtained with duty cycles higher than 50% is smooth, while with lower duty cycles the deposit obtained is more nodular-like even at the same thickness.

### 7.3.2 Cross-section characterisation

The optical cross-sections of multilayered coatings on copper substrate are shown in Figure 7.42. The multilayered structure was clearly revealed after etching. The bright layers were Sn-Co alloys, which was less etched due to their higher corrosion resistance in the ferric chloride etchant. The dark layers were pure tin layers and were etched to a greater extent. The individual layers in all these coatings were continuous, though not flat and smooth, and the corresponding interfaces between layers were distinct. The cross-section of multilayer coatings with thinner individual layer thicknesses (0.5 \(\mu\)m) is shown Figure 7.43. Since it became much more difficult to etch the sample with such thin individual layers, the multilayered structure was not as clearly revealed as in the coatings consisting of thicker individual layers. This phenomenon may be attributed to the increased corrosion resistance of the multilayer coating with very thin layers, or the incomplete coverage of individual layers on the top of each other, which leads to the mixing of interfaces between layers.
According to the design, the coatings in Figure 7.42 should have the thickness configuration of 1 µm Sn-Co alloy layers followed by 1, 2, and 3 µm Sn layers, respectively. Although the actual thicknesses of individual layers did not follow the theoretical ones precisely, they varied proportionally with the latter. With some modifications of the electroplating time, there should be no difficulty in depositing multilayer coatings to a pre-determined format.

Figure 7.42 also indicates that the difference between the substrate roughness of these three samples was negligible, and the electrodeposition characteristics of tin layers should be responsible for the increase of the surface roughness of the multilayer coatings with increase in the thickness of individual tin layers, as described in Section 7.3.2. As can be seen in Figure 7.42(c), the formation of coarse nodules was initiated during the deposition of the first layer of tin, and was further amplified during the subsequent deposition of the remaining layers. This characteristic may be related to the fact that the applied current density (0.5 A/dm²) for the deposition of tin layers was close to the limiting current density of tin under the conditions studied, as indicated by the potentiodynamic polarisation measurement in the following Section 7.5. The instability of the surface and the consequent formation of nodules were also observed by Menezes et al. [147] during the deposition of Cu/Ni multilayer coatings.

The cross-section of the multilayered coatings deposited on plain bearings is shown in Figure 7.44. Although there is no doubt that the multilayered structure was also obtainable on plain bearings, the control of the individual layer thickness was more difficult. The thickness of the tin layers was not uniform throughout the coating, with the first layer of tin being thicker than the others.

### 7.3.3 Composition profile

X-ray elemental mapping was used to study the composition modulation of a multilayer coating deposited on the surface of a plain bearing with a nickel barrier layer. Figure 7.45 shows the location where the elemental mapping was carried out. The mapped elements were nickel, tin and cobalt. As can be seen from the distribution of cobalt (Figure 7.46 (b)),
there exists apparent composition difference between these bright and dark layers, with the bright layers rich in cobalt. From the distribution of nickel, it is found that there is a distinct interface between the multilayer coating and the nickel barrier layer. Point composition analysis was only applicable in the first dark layer, which was found to be consisted mainly of tin. The bright sublayers and the other dark sublayers are too thin, therefore some signals are inevitably collected from the neighbouring layers, which interfere in the point composition analysis. Due to this resolution limitation of the equipment, no accurate composition of each sublayer was possible using the SEM.

### 7.3.4 Microhardness

Microhardness tests were only conducted with single layer tin/tin-cobalt alloy coatings. Table 7.14 gives the microhardness and the composition of single layer coatings obtained at the current density of 0.5 A/dm$^2$ from solutions containing various concentrations of Tween 20. It can be seen that these coatings mainly consisted of tin and their microhardness values remained around 13HV and were not affected by the concentration of Tween 20.

For single layer tin-cobalt alloy deposits, their microhardness is much more sensitive to the variations in the concentration of Tween 20 added to the solution and the applied current waveform. Tables 7.15 and 7.16 give the microhardness and the composition of tin-cobalt alloy deposits under these different conditions. The electrodeposition was always carried out at the same average current density of 3 A/dm$^2$. The cobalt content in the solution was 15%. The microhardness of single layer tin-cobalt alloy deposits increases with increasing concentration of Tween 20 and the off-time of the pulsed current. Taking the deposit composition into consideration, it can also be deduced from Tables 7.15 and 7.16 that the microhardness of single layer tin-cobalt alloy deposits is, in general, a function of the cobalt content in the deposits. Factors increasing the cobalt content in the deposits, such as a higher concentration of Tween 20 and a lower duty cycle of the pulsed current waveform, also lead to an increase in the microhardness value.
Table 7.14 Microhardness of single layer tin coatings obtained at various concentration of Tween 20

<table>
<thead>
<tr>
<th>Tween 20 ml/l</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt in deposits wt.%</td>
<td>0.3</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HV (5g load)</td>
<td>13</td>
<td>11</td>
<td>14</td>
<td>13</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 7.15 Composition and microhardness of single layer tin-cobalt alloy deposits from solutions with various concentration of Tween 20

<table>
<thead>
<tr>
<th>Tween 20 ml/l</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt in deposits wt.%</td>
<td>6</td>
<td>9</td>
<td>10</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>HV (5g load)</td>
<td>175</td>
<td>214</td>
<td>480</td>
<td>391</td>
<td>653</td>
</tr>
<tr>
<td>HV (10g load)</td>
<td>163</td>
<td>-</td>
<td>372</td>
<td>356</td>
<td>405</td>
</tr>
</tbody>
</table>

Table 7.16 Composition and microhardness of single layer tin-cobalt alloy deposits obtained with different current waveforms

<table>
<thead>
<tr>
<th>Current waveform</th>
<th>DC</th>
<th>PC1-1ms</th>
<th>PC1-2ms</th>
<th>PC1-4ms</th>
<th>PC1-9ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt in deposits wt.%</td>
<td>6</td>
<td>7</td>
<td>9</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>HV (5g load)</td>
<td>91</td>
<td>218</td>
<td>214</td>
<td>391</td>
<td>335</td>
</tr>
</tbody>
</table>

7.3.5 Fatigue tests

7.3.5.1 Fatigue strength of multilayered overlays

The fatigue strengths of Sn-Co/Sn multilayer coatings electrodeposited on plain bearings from two solutions with different cobalt contents are shown in Tables 7.17 and 7.18, respectively. In Table 7.17, the thicknesses of the individual layers were varied systematically whilst the ratio of the thickness of the Sn-Co alloy layer to that of the Sn layer remained constant at 1:2. There is no significant difference between the fatigue...
### Table 7.17 Fatigue strength of Sn-Co alloy multilayer coatings electrodeposited on plain bearings from a solution containing 15wt.% cobalt

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Thickness configuration</th>
<th>Fatigue strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alloy layers µm</td>
<td>Tin layers µm</td>
</tr>
<tr>
<td>723-1-A/B</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>723-2-A/B</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>723-3-A/B</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>723-4-A/B</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

i. A or B in the sample codes stands for the position of a bearing in the electroplating jig when two bearings were electrodeposited together. Bearing A stood above B (See Figure 6.3).

### Table 7.18 Fatigue strength of Sn-Co alloy multilayer coatings electrodeposited on plain bearings from a solution containing 20wt.% cobalt

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Thickness configuration</th>
<th>Fatigue strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alloy layers µm</td>
<td>Tin layers µm</td>
</tr>
<tr>
<td>1112-4-A/B</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1112-8-A/B</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1112-6-A/B</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>1113-2-A/B</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

i. A or B in the sample codes stands for the position of a bearing in the electroplating jig when two bearings were electrodeposited together. Bearing A stood above B (See Figure 6.3).

ii. Sample group 1112-8 differs from 1112-4 by starting with a 2 µm tin layer, which is then followed by the normal stacking sequence of Sn-Co/Sn

iii. For sample group 1113-2, the alloy layers were deposited using a pulsed current waveform with an off-time of 4 ms, whilst for other groups the alloy layers were deposited with an off-time of 9 ms.
strength values for those samples deposited from the solution with a cobalt content of 15%,
which were always around 69 MPa. However, for the multilayered coatings from the
solution containing 20% cobalt, higher fatigue strength values were obtained, which were
around 83 MPa. A common feature for all of these multilayer coatings tested is that the
fatigue strength showed no evident dependence on the individual layer thickness
configuration.

7.3.5.2 Characterisation of multilayered overlays after fatigue testing
The surface morphologies of multilayered overlays after fatigue testing were examined
using the SEM. Figure 7.47 shows a multilayered sample which failed at 90MPa. It
indicates that the multilayered overlay has fatigue cracked in the typical failure mode
observed for monolithic overlays, which has been described in Section 2.3. The loss of
areas of overlay material and the formation of pits or trenches were due to the fatigue
cracking. This assertion may be further confirmed by the observation of a loose piece of
overlay which still remains in place (Figure 7.47(b)). In the vicinity of this loose piece, a
fatigue pit has formed and a fatigue crack linking to another pit (not on micrograph) can
also be observed.

For the multilayered overlay, it might be thought that the fatigue cracks may change their
propagation direction and perhaps extend parallel to the interface between individual layers
due to the interface effects. This characteristic could manifest itself by the formation of
steps at different depth in the fatigue pits. In effect, fatigue pits with steps were only
observed occasionally on the fatigue cracked multilayer overlays (for example, as indicated
by the arrow in Figure 7.48(a)). Most of the fatigue pits observed exhibited a sharp and
smooth wall on one side and a ragged wall on the other (Figure 7.48(b)). However, closer
examination of the bottom of the fatigue pits provided some different evidence. As shown
in Figure 7.49, there exist two types of areas in the fatigue pits. One has a crystalline
morphology, and the other appears much rougher. Compositional analysis by EDX
indicated that the crystalline areas consisted of tin and cobalt, whilst in the rough areas
only tin was detected. This suggests that the loose piece of overlay separated from the
bearing at different interfaces between individual layers, which was an indication that the
fatigue cracks may well have deflected during their propagation.
The deflection of fatigue cracks in the multilayer overlays was further confirmed by the examination of the cross-sections of plain bearings after fatigue tests. As shown in Figure 7.50 (a), the fatigue crack was stopped at the interface, forming branches after it has penetrated the first few sublayers. For more severe fatigue cracked areas, steps are revealed clearly in the corresponding fatigue pit (Figure 7.50(b)). Figure 7.50(c) shows the multilayered structure of the overlay within the area without fatigue cracks. There are only five layers left, with the first tin layer being worn away. It is also worth noting that the deflection of fatigue cracks was observed not only on the cross-sections of plain bearings with higher fatigue ratings, e.g. 83 and 90 MPa (Figure 7.50), but also on the cross-sections of plain bearings with a lower fatigue strength value of 69 MPa (Figure 7.51).

7.3.6 Internal stress

7.3.6.1 Electrolyte composition dependence

The internal stress of deposits from two electrolytes which contained 15wt.% and 20wt.% cobalt metal, respectively, was studied using the bending strip method. The development of internal stress in the deposits with time (or the deposit thickness) was monitored in-situ by the deflection of the extended copper wire (See Figure 6.4). As indicated by Figure 7.52, during the deposition of tin-cobalt alloys at 3A/dm² by direct current (DC) or pulsed current (PC), the deflection increases gradually with the progress of deposition, whilst its sign shows a strong dependence on the electrolyte composition. For the electrolyte with a metal content of 15wt.% cobalt, the deflection is negative (or away from the anode) indicating the internal stress in the deposit is compressive. However, the deflection turns positive (or towards the anode) when the cobalt metal content in the electrolyte is 20wt.%.

This means the internal stress in the deposit from this solution is tensile in nature.

Another interesting observation was made on the internal stress development after the electrodeposition was finished. For the electrolyte with 15% cobalt, the deflection of the extended copper wire remained unchanged after the current was switched off and therefore there was no further development of internal stress in the deposits. On the contrary, for the electrolyte with 20% cobalt, the deflection of the extended copper wire exhibited a sharp increase (about 1mm) shortly after the current was switched off and a stable deflection
could only be obtained a few minutes later. This suggests that there was still an increase in the internal stress in the tin-cobalt alloy deposits after the deposition was finished.

For the deposition of pure tin at 0.5A/dm², the average internal stress in the deposit is much smaller in magnitude compared with that in the single layer tin-cobalt alloy deposits (Table 7.19). The deflection of the extended copper wire was normally around 1mm. Therefore the variation of the deflection with deposition time was very difficult to trace. Only the average internal stress of the pure tin deposit was available by measuring the deflection at the free end of the bent strip cathode after it was withdrawn from the electrolyte. Unlike the single layer alloy deposits, the internal stress in the pure tin deposit was always compressive, and does not change its sign with variations in the cobalt content in the electrolyte.

Table 7.19 Average internal stress in single layer coatings obtained under different electroplating conditions

<table>
<thead>
<tr>
<th>Cobalt metal content in the solution</th>
<th>Average internal stress</th>
<th>MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn-Co alloy</td>
<td>Pure tin</td>
</tr>
<tr>
<td></td>
<td>DC</td>
<td>PC1-4ms</td>
</tr>
<tr>
<td>20%</td>
<td>60</td>
<td>81</td>
</tr>
<tr>
<td>15%</td>
<td>-50</td>
<td>-32</td>
</tr>
</tbody>
</table>

Figure 7.53 illustrates the deflection of the extended copper wire during the deposition of tin-cobalt alloy multilayer coatings. The deflection was measured at the end of the deposition of each sublayer. For the electrolyte with a cobalt metal content of 15wt.%, the deflection increases continuously in the negative direction with alternating deposition of the sublayers. According to the formula given by Perakh [177] and Sotirova et al. [178], the instantaneous internal stress ($\sigma_i$) in the last sublayer is proportional to the alteration of the deflection ($\Delta\delta$) at the free end of the bent trip cathode after the last sublayer is deposited. Since $\Delta\delta$ is always negative during the deposition, the instantaneous internal stress
stresses in the both sublayers must have the same sign, which is compressive. This is consistent with the result for their single layer coatings.

For the electrolyte with a cobalt metal content of 20 wt.%, the strip cathode bent towards the anode in a zigzag manner (forwards and backwards). As shown in Figure 7.53(b), the deflection of the extended copper wire increases during the deposition of tin-cobalt alloy sublayers, but it decreases after pure tin sublayers are deposited. From this observation it can be deduced that the change in the deflection ($\Delta \delta$) at the free end of the bent strip cathode is positive due to the deposition of tin-cobalt alloy sublayers, and negative due to the deposition of pure tin sublayers. Therefore, the instantaneous internal stress with which the tin-cobalt alloy sublayers are deposited is tensile, whilst the instantaneous internal stress with which the pure tin sublayers are deposited is compressive. Again, this result reveals that the nature of the instantaneous internal stress in both sublayers corresponds to that of their own single layer coatings. The change of the substrate during the deposition of multilayer coatings does not lead to an alteration of the nature of the instantaneous internal stress in the sublayers.

The values of the average internal stress in the multilayer coatings deposited from the two electrolytes are given in Table 7.20. It can be seen that the average internal stress values of the multilayer coatings are situated between the stress values for equivalent single layer coatings corresponding to both sublayer compositions.

<table>
<thead>
<tr>
<th>Cobalt metal content in electrolyte</th>
<th>Average internal stress MPa</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn</td>
<td>Multilayer coatings</td>
</tr>
<tr>
<td>15 wt.%</td>
<td>-15</td>
<td>-37</td>
</tr>
<tr>
<td>20 wt.%</td>
<td>-15</td>
<td>22</td>
</tr>
</tbody>
</table>
7.3.6.2 Effect of current waveforms

Although pure tin sublayers were always produced at a current density of 0.5 A/dm$^2$ by direct current in this research, tin-cobalt alloy sublayers were deposited under either direct or pulsed current conditions at the same average current density of 3 A/dm$^2$. The resulting effects from such variations in the current waveform on the average internal stress within the multilayer coatings is illustrated in Figures 7.54 and 7.55. All the multilayer coatings reported had 12 sublayers each of which had a thickness of approximately 1μm. For comparison, Figures 7.54 and 7.55 also give the effect of current waveforms on the average internal stress in the single layer coatings with comparable overall thickness to that of the multilayer coatings. For the solution with 15 wt.% cobalt in metal content (Figure 7.54), with increase of the off-time from zero (direct current) to 9ms or decrease of the duty cycle from 100% to 10%, the compressive internal stress within both the single layer and the multilayer coatings decreases. Meanwhile the value of the average internal stress within the multilayer coating is always located between the stress values of the corresponding single layer coatings. Higher compressive internal stress was found in the single layer tin-cobalt alloy deposits for all the current waveforms, except for the pulsed current with an off-time of 9ms (PCI-9ms). In the latter case, the compressive internal stress in the single layer tin-cobalt alloy coating obtained was only about 6MPa, whilst in the single layer pure tin coating it was about 15 MPa.

For the solution containing 20 wt.% cobalt as metal (Figure 7.55), the average internal stress within single tin-cobalt layers is always tensile and has a maximum value at a duty cycle of 33% (PCI-2ms). On the other hand, most of the multilayer coatings obtained have zero average internal stress. Slight tensile stress was found only in the cases of PCI-4ms and PCI-9ms. This implies that in most of the cases the tensile stress within the tin-cobalt alloy sublayers has been completely neutralised by the compressive stress within the subsequent pure tin sublayers. Note that for those multilayer coatings with zero average internal stress, the strip cathode did not remain in a stationary state during the whole deposition process. Instead, it oscillated near its original position in the solution. It bent towards the anode slightly during the deposition of tin-cobalt alloy sublayers and fell back to its original position after the pure tin sublayers were deposited.
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7.3.6.3 Thickness configuration

To study the effect of the thickness configuration of the multilayer coatings on the average internal stress, the thickness of pure tin (or tin-cobalt alloy) sublayers were varied from 0.5μm to 3μm whilst keeping the thickness of the other component at a constant of 1μm. From Figure 7.56, it can be seen that in the solution containing 15 wt.% cobalt, the average internal stress in the multilayer coatings becomes more compressive with increase in the thickness of tin-cobalt alloy sublayers. This reflects the increased influence of the alloy sublayers. As to the effect of the thickness of the pure tin sublayers, the general trend is that the compressive internal stress is lower in the multilayer coating with thicker pure tin sublayers.

For the solution containing 20 wt.% cobalt, the effect of the thickness configuration of the multilayer coatings on the average internal stress is illustrated in Figure 7.57. The tensile stress in the tin-cobalt alloy sublayers of 1 μm is totally offset by the compressive stress in the pure tin sublayers when the thickness of the latter is greater than 2 μm (curve (a)). The effect of the thickness of the alloy sublayers was not studied in full (curve (c)). Although the average internal stress in multilayer coatings with an alloy sublayer of 1 or 2 μm is the same, it is expected that with increase in the thickness of the alloy sublayer, its influence will become dominant, and consequently the tensile internal stress will increase. Curve (b) in Figure 7.57 shows the variation of the average internal stress in the multilayer coatings with equal sublayer thickness. The stress value exhibits a peak at 1 μm. This might be explained by that the stress in the very thin sublayers, i.e. 0.5 μm, is not fully developed and thus the average value of the multilayer coating is zero. On the other hand, when the sublayers are thicker than 1 μm, the pure tin sublayers, which are compressive, become more effective in countering the tensile stress in the alloy sublayers. As a result the average internal stress is decreased.

7.3.6.4 Effect of frequency

Investigations on the effect of frequency of the applied pulsed current on the average internal stress were carried out with single layer tin-cobalt alloy deposits from the solution containing 15 wt.% cobalt (as metal). As shown in Figure 7.58, the internal stress in the coatings obtained at a frequency of 333 Hz is compressive. The decrease in frequency leads to a transition from compressive to tensile stresses. The stress values increase with this decrease in the frequency. In addition, it was also observed that the internal stress in
tin-cobalt alloy deposits obtained at various frequencies builds up with electroplating time in different ways. As illustrated by the deflection of the extended copper wire in Figure 7.59, the deflection at the frequency of 333 Hz is always negative. (Note that a deflection is defined as negative when the cathode bends away from the anode. The corresponding internal stress in the deposit is compressive. Conversely, a deflection is defined as positive when the cathode bends towards the anode. The internal stress in the deposit is tensile). For the frequencies of 33 Hz and 66 Hz, the deflection is negative initially, but it becomes positive after the deposit is sufficiently thick. At the frequency of 6 Hz, the deflection is always positive. These observations indicate that there is a change of the stress state (from compressive to tensile) in the deposits obtained at the frequencies of 33 and 66 Hz during the deposition. The sharp increase of the last data point on the curves for 6 Hz and 33 Hz is due to the phenomenon mentioned earlier, i.e. a fast increase in the deflection after the current is switched off.

7.3.6.5 Effect of Tween 20

The effect of Tween 20 on the internal stress was studied with single layer coatings in the solution with a cobalt metal content of 15wt.%. It was found that under direct current conditions, Tween 20 has no effect on the average internal stress in the deposit produced at 3 A/dm² (Figure 7.60). However, the value of the compressive internal stress in deposits obtained at a current density of 0.5 A/dm² decreased gradually with increase of the quantity of Tween 20 added to the solution. Under pulsed current conditions (Figure 7.61), a large quantity of Tween 20 also leads to a decrease in the compressive stress within the alloy deposits obtained.

7.4 Potentiodynamic polarisation studies

7.4.1 Effect of Tween 20

7.4.1.1 Deposition of tin

Figure 7.62 shows the potentiodynamic polarisation curves for the deposition of tin. It can be seen that without the addition of Tween 20, no appreciable current was observed until the potential was swept to about -620mV. After a sharp increase to a peak value, the current density drops slightly and then comes to a slow and steady increase. At the
potential of about -1200mV, the current starts to increase markedly again, with hydrogen bubbles evolving from the cathode. The limiting current density for the deposition of tin was about 1A/dm².

Addition of Tween 20 does not change the potential for the onset of the deposition reaction, but it changes the overall shape of the polarisation curve. At first, there appears an apparent peak at around -700mV on the polarisation curve. Secondly, after the peak the current density drops sharply to a minimum and then it starts to rise again and reaches a limiting current density of about 0.5A/dm².

The changes in the polarisation curves caused by adding Tween 20 indicate that Tween 20 has a strong inhibiting effect on the deposition of tin and it starts to take effect shortly after the initiation of the deposition reaction for tin. On the other hand, the polarisation curves for different concentrations of Tween 20 merge together and no significant concentration effect is found. This implies that the effect of Tween 20 has reached its maximum even at the concentration of 0.1ml/l.

7.4.1.2 Deposition of cobalt
The effect of Tween 20 on the deposition of cobalt is slight (Figure 7.63) and therefore not conclusive, although it seems that with increasing concentration of Tween 20, the polarisation curve shifts slightly to the more positive potentials. The potential at which cobalt starts to deposit falls within the range from -850mV to -950mV.

7.4.1.3 Deposition of tin-cobalt alloys
The polarisation curve for the deposition of tin-cobalt alloy without addition of Tween 20 is given in Figure 7.64. For the purpose of comparison, the polarisation curves for the deposition of tin and cobalt alone are marked, as well as the ‘resultant’ curve (dashed line) which is obtained by adding up the ordinates of the individual polarisation curves for tin and cobalt. Although the tin-cobalt alloy polarisation curve is not simply an additive one, it can be seen that the deposition of tin dominates at less negative potentials, and considerable codeposition of cobalt is observed only after the potential is more negative than about -1000mV.
The effect of Tween 20 on the deposition of tin-cobalt alloys is shown in Figure 7.65. The polarisation with the addition of Tween 20 is greatly increased. As a consequence, the limiting current density for the deposition of tin is decreased almost by half (See Figure 7.62), whilst the potential for the codeposition of tin and cobalt (and also the evolution of hydrogen) at the same current density is shifted by about 400mV in the more negative direction.

7.4.1.4 Potential sweep rate and substrate effects

Investigations were carried out to reveal whether the appearance of a peak in the polarisation curves associated with the addition of Tween 20 were due to the deposition of tin or other factors such as the potential sweep rate and the cathode material. As shown in Figure 7.66, the appearance of the peak is independent of the potential sweep rate. There still exists a peak even when the potential sweep rate is 0.5mV/sec. On the other hand, the potential corresponding to the peak shifts slightly to more negative potentials and the height of the peaks increases with increase in the potential sweep rate. Furthermore, in order to eliminate the effect of potential sweep rate completely, potentiostatic polarisation was carried out. The potential of the working electrode was maintained at different constant values for about 5 minutes. The time responses of the current at each electrode potential were recorded and are given in Figure 7.67. The corresponding polarisation curve obtained is shown in Figure 7.68. As can be seen from Figure 7.67, a steady state has been attained at the end of each run of the experiment. However, even under these conditions, the current density peak still presents itself on the polarisation curve (Figure 7.68). Therefore there is no doubt that the appearance of a peak on the polarisation curve of tin or tin-cobalt alloys with addition of Tween 20 is not due to the potential sweep rate, although it does have some effects on the position and the height of the peak.

Cathodic polarisation curves using different cathode materials are shown in Figure 7.69. It can be seen that the peak is always present irrespective of what cathode material was employed, but the cathode material does affect the details of the polarisation curves, particularly when lead was used as the cathode. In addition, the rest potential of these cathode materials in the electrolyte tested decreases in the order of copper (-145mV), nickel (-443mV), tin (-452mV), and lead (-570mV).
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To further study the effect of the cathode material and the potential sweep mode, the copper substrate was first deposited with a layer of tin-cobalt alloy at a constant potential of -1700mV for 3 minutes. The electrode potential was then swept in the positive (anodic) direction at the same rate of 2 mV/sec. The polarisation curve recorded is illustrated in Figure 7.70. It is interesting to note that the current density peak is still present even when the potential was swept in the opposite direction. The height of peak is somewhat lower. Data on this figure further indicates that the rest potential of deposited tin-cobalt alloy in the test electrolyte is about -570mV and an anodic current peak appears at the electrode potential of about -280mV.

7.4.2 Mass transport in sulfate/gluconate baths

7.4.2.1 Effect of agitation

The effects of agitation on the deposition of tin-cobalt alloys from the solution with or without addition of Tween 20 are shown in Figures 7.71 and 7.72, respectively. As can be seen from Figure 7.71, when there is no Tween 20 added, the deposition reaction is markedly enhanced by the application of agitation and thus no mass transport limiting plateau was observed. Figure 7.71 also exhibits an apparent depolarising effect of agitation on the hydrogen evolution reaction. However, for the solution with more than 4ml/l Tween 20, the effect of agitation is not so straightforward but shows different effects at different points on the polarisation curves (Figure 7.72). For the current density peak, the effect of agitation is as considerable as in the solution without Tween 20. After the peak, agitation still shows some enhancing effect on the deposition reaction, but the extent is much less in comparison with that in the solution without Tween 20 in Figure 7.71.

Figures 7.71 and 7.72 also indicate some common features of the effect of agitation in the solution with or without Tween 20. That is, the application of agitation does not alter the potential at which the deposition of tin commences, and the effect of agitation levels off with increasing agitation, which is supported by the fact that the polarisation curves merge together after a certain agitation level was attained.

The polarisation curves for the deposition of tin alone using different agitation levels are shown in Figure 7.73. As can be seen, the effect of agitation on the deposition of tin is
similar to that on the deposition of tin-cobalt alloys. For the deposition of cobalt alone, the limiting current density plateau observed in the stationary solution totally disappears with the application of agitation (Figure 7.74), due to both the depolarising effect of agitation on hydrogen evolution reaction and the small overpotential required for the evolution of hydrogen on cobalt. As a result, it is difficult to evaluate the effect of agitation on the limiting deposition rate of cobalt on the basis of polarisation curves.

7.4.2.2 Effect of the concentration of the main metal salts

Figures 7.75 and 7.76 illustrate the effect of concentration of the main metal salts, namely stannous sulfate and cobalt sulfate, on the tin-cobalt alloy cathodic polarisation curves. With increase in the concentration of stannous sulfate in the electrolyte with constant cobalt ion concentration (Figure 7.75), the limiting current density for the deposition of tin increases continuously. At 9g/l stannous sulfate, there appears a second limiting current plateau, indicating the deposition of cobalt dominates so as to reveal the polarisation characteristics of cobalt alone.

As shown in Figure 7.76, with increase in the concentration of cobalt sulfate in the electrolyte with constant stannous sulfate, no effect was observed before the second current rise from the limiting current plateau of tin. The major difference between these polarisation curves caused by the concentration variation of cobalt ions is that the second current rise becomes more and more sharp and discernible, whilst the following part of the polarisation curves shifts towards less negative potentials showing apparent depolarisation effect. Therefore, it is reasonable to conclude that only tin is deposited initially, and codeposition of cobalt with tin accounts for the current rise from the limiting plateau of tin.

7.4.2.3 Effect of the concentration ratio of tin to cobalt ions

Keeping the total number of moles of tin(II) and cobalt ions in the solution constant, i.e. 0.25 mol/l, their concentration ratio was varied to investigate the corresponding effect on the polarisation characteristics. In this way, the interference from the degree of complexing of tin and cobalt ions can be eliminated, because the ratio of the complexing agent to the total concentration of tin and cobalt ions was not changed. As can be seen from Figure 7.77, the height of the current density peak and the limiting plateau for the reduction of tin increases, whilst the polarisation for the codeposition of cobalt increases apparently, with increase in the ratio of $[\text{Sn}^{2+}]/[\text{Co}^{2+}]$ from 0.7 to 4.5.
7.4.3 Stability of gluconate complexes

7.4.3.1 Effect of pH
In a solution containing complexing agent, variations of pH cause shifts in the equilibrium between the various kinds of complex species present. The composition and thus the stability of a complex are a function of the pH value, particularly when its stability constant is small. The correlation between the degree of complexation and the variation of pH could be manifested electrochemically, i.e. by the variation in the deposition potential of metals and consequently in their ease of deposition.

Figures 7.78 and 7.79 show the influence of pH on the polarisation characteristics of tin and cobalt without addition of Tween 20, respectively. With increase in pH the negative shifts in the deposition potential of tin and cobalt are clearly exhibited, indicating the reducible species become more and more stable. On the other hand, the limiting current densities for tin and cobalt decrease continuously with increasing pH value of the electrolyte. It can also be seen from these figures that the polarisation of hydrogen evolution decreases with increasing solution acidity. The limiting current density plateau of cobalt reduction disappears at pH 1, where it has been completely masked by the partial polarisation curve for hydrogen evolution.

The effect of pH on the polarisation of tin-cobalt alloy from the solution with and without Tween 20 is illustrated in Figures 7.80 and 7.81. The result is quite similar to that of tin and cobalt alone, apart from that the shape of the curves at pH higher than 6 presents some irregularities, i.e. the appearance of a shoulder on the curve before the current density peak and the limiting current plateau.

7.4.3.2 Effect of sodium gluconate
Another factor which is expected to affect the stability of gluconate complexes of tin and cobalt ions is the concentration of the complexing agent itself, i.e. sodium gluconate. Figure 7.82 illustrates the effect of sodium gluconate on the reduction of tin alone. There is no marked influence on the polarisation curves with different quantities of sodium gluconate. However, the chemical stability of the gluconate complex of tin(II) ions must
have been increased with increase in the concentration of sodium gluconate. As proof, in
the electrolyte containing 36g/l stannous sulfate, hydrolysis of tin(II) could not be
completely inhibited by the formation of the gluconate complex when the concentration of
sodium gluconate is less than 60g/l. The solution became cloudy even after careful
filtration of insoluble species. Due to the hydrolysis of tin(II) ions, no data was obtainable
for the reduction of tin(II) ions from the simple salt electrolyte at pH 4.

For the reduction of cobalt ions alone (Figure 7.83), the polarisation curve from the simple
salt electrolyte was possible because the solubility constant of Co(II) hydroxide (Co(OH)₂)
is much higher than that of tin(II) hydroxide (Sn(OH)₂), and no precipitation took place in
the solution at pH 4. Addition of sodium gluconate shifts the deposition potential of cobalt
towards more negative values. This implies the formation of gluconate complexes of cobalt
ions. However, like the reduction of tin alone, the effect of the concentration of sodium
gluconate does not show great effect on the reduction of cobalt alone. The changes in the
limiting current density and the deposition potential with the concentration of sodium
gluconate are within the range of experimental error.

The effect of the concentration of sodium gluconate in the alloy electrolyte is illustrated in
Figure 7.84. As with its effect on the reduction of tin and cobalt alone, the codeposition of
tin and cobalt is barely affected by the variation of the concentration of sodium gluconate.

7.4.4 Effect of Boric acid

Figures 7.85 and 7.86 illustrate the effect of boric acid. Without the addition of Tween 20,
little difference can be observed between the polarisation curves for the different quantities
of boric acid. After 4ml/l Tween 20 was added into the solution, the effect of boric acid
becomes obvious. Without boric acid, the sudden drop of the current due to the presence of
Tween 20 takes place at much less negative potential and the degree of the current drop is
less than that with addition of boric acid. However, the concentration of boric acid does not
seem to have any significant influence on the general polarisation.
CHAPTER 7 RESULTS AND DISCUSSION

7.4.5 Solution stability

Due to the well-defined limiting current plateau for the reduction of tin on the polarisation curve, a potentiodynamic polarisation study was employed to reveal the chemical stability of the sulfate/gluconate electrolyte. A volume of 300 ml electrolyte of pH 4 was prepared and was characterised by polarisation studies. The electrolyte was then stored in a beaker for 3 months. After adjusting the pH value of the aged solution to 4, it was topped up to 300 ml to compensate for the loss of water due to evaporation and was subjected to a polarisation study again. The results are shown in Figure 7.87. The limiting current plateau for the reduction of tin was decreased markedly after the electrolyte was aged for 3 months, suggesting that a large proportion of tin(II) had been oxidised to tin(IV). As to the cobalt ions in the electrolyte, it seems that they are quite stable. On the polarisation curve of the aged solution there appears a second limiting plateau and this plateau is attributable to the reduction of cobalt.

7.4.6 Anodic polarisation

The anodic behaviour of the tin-cobalt alloy deposited at a constant potential of -1700mV on a copper substrate is illustrated in Figure 7.88. The potential scan was started from the open-circuit potential, which was about -560mV. The alloy deposit was actively dissolved when the electrode potential was scanned positively and then passivation was observed at the potential of -420 mV. Within a wide potential range from -140mV to 1400mV, the anodic current was very small.

7.5 Formation of tin(II) hydroxide and its effect

From section 7.2.2.4, it was found that there is a critical cobalt content in the electrolyte, below which the deposition of tin-cobalt alloys becomes very difficult as the deposit tends to form powdery dendrites within the operating current density range (Figure 7.24). According to Survila and co-authors [179], the oversaturation with insoluble tin(II) hydroxides on the surface of the cathode was detrimental to the deposition process of tin-cobalt alloys. It was initially thought that the problem was also caused by the formation of insoluble tin(II) hydroxides (Sn(OH)\(_2\)) on the surface of the cathode due to the rapid
increase in pH value at the cathode surface due to the concurrent evolution of hydrogen, since the formation of tin(II) hydroxides may become more severe with decrease of the cobalt content and increase of tin(II) content in the electrolyte. This proposal is reasonable because the solubility product (K\text{sp}) of Sn(OH)\textsubscript{2} is very small, only 5×10\textsuperscript{-26} [180] (pK\text{sp} = 25.3 at 25°C) and, therefore, tin(II) is prone to hydrolysis forming insoluble hydroxides.

To verify this presumption, titration experiments were carried out so that the variation of the pH value with the addition of 2.5 M sodium hydroxide solution into the electrolyte was recorded and the pH value at which colloidal precipitates was formed in the electrolyte was identified. As can be seen from Figure 7.89, with decrease in the cobalt metal percentage in the electrolyte, i.e. an increase in concentration of tin(II) ions, the pH value at which colloidal precipitates were observed decreases. This result seems in good agreement with the presumption and did provide some evidence that the formation of hydroxide precipitates in the electrolyte of higher tin(II) ion concentration is easier and needs less pH increase. However, at this stage, it is not certain whether these precipitates are tin(II) hydroxide or a mixture of tin(II) and cobalt(II) hydroxides, as the titration was conducted in alloy electrolytes.

Figure 7.90 shows the titration curves for electrolytes containing different concentrations of stannous sulfate and also 120 g/l sodium gluconate, 30 g/l boric acid, and 20 g/l sodium sulfate. The pH value corresponding to the formation of hydroxide precipitates decreases with increasing the concentration of stannous sulfate. However, during the titration of electrolytes containing different quantities of cobalt sulfate no precipitation was observed even at the pH value of 10, as shown in Figure 7.91. The formation of a gluconate complex with cobalt(II) and the much higher solubility product of Co(OH)\textsubscript{2} (K\text{sp} = 1×10\textsuperscript{-16} [180]) might be responsible for the difference between tin and cobalt electrolytes. From the titration curves of the electrolytes for individual metals it was found that the formation of a precipitate in the alloy electrolytes is due to the hydrolysis of tin(II) ions.

Although the formation of tin(II) hydroxides at lower pH values for alloy electrolytes containing higher concentration of tin(II) sulfate seems to explain the difficulty in producing acceptable tin-cobalt alloy deposits from these electrolytes, contradictory results were obtained when the effects of boric acid and sodium gluconate were considered. As can be seen from Figure 7.92, without the addition of boric acid no precipitation occurs.
even under highly alkaline conditions. After the addition of boric acid, it is interesting to note that the pH value for the formation of insoluble tin(II) hydroxides decreases with increase in the concentration of its addition. This result cannot explain the fact that the addition of boric acid improves the quality of the alloy deposits and its concentration in the solution does not have an appreciable effect on the deposition of tin-cobalt alloys. Similarly, the increase in the critical pH value with the concentration of sodium gluconate (Figure 7.93) makes the proposal based on the formation of insoluble tin(II) hydroxides more doubtful, as it has been established that with an increase in the concentration of sodium gluconate the deposition of acceptable alloy deposits becomes more difficult, whilst the concentration of sodium gluconate only has negligible influence on the cathodic current efficiency (Figure 7.35). Therefore, the formation of insoluble tin(II) hydroxides during the electrodeposition of tin-cobalt alloy either does not occur as the pH value near the cathode does not change significantly, or their formation is not responsible for the formation of dendrites. In addition, Figures 7.92 and 7.93 indicate that both boric acid and sodium gluconate have some buffering ability. They could, to some extent, stabilise the pH value of the solution so that the variation of pH, with the addition of the same amount of sodium hydroxide solution to the electrolyte, decreases in their presence.

7.6 Summary of results and discussion

7.6.1 Deposition of tin-cobalt alloys

7.6.1.1 Complexing
The electrodeposition of alloys involves the simultaneous discharge of the cations of two or more metals. According to Brenner [181], for the simultaneous discharge of metal ions to occur and thus produce a satisfactory alloy, their individual equilibrium potential in the system under discussion should not be too widely apart so that the deposition potential of the less noble metal can be attained without employing an excessive current density. The equilibrium potential of a metal in its own simple salt solution is given by the Nernst equation as:

$$E = E^o + \frac{RT}{nF} \ln \alpha_{M^{n+}}$$  

(7.1)
where $E^*$ is the standard electrode potential and $\alpha$ is the activity of the metal ion $M^{n+}$ in solution.

As far as the deposition of tin-cobalt alloys is concerned, the standard electrode potentials for the parent metals of tin-cobalt alloys are [181]

$$E_{\text{Sn}^{2+}/\text{Sn}}^* = -0.136 \ V$$

$$E_{\text{Co}^{2+}/\text{Co}}^* = -0.277 \ V$$

respectively. The difference between these two values is so small that one would not expect any difficulties in the deposition of tin-cobalt alloys from a solution made up of their simple salts. However, in practice problems occur on electrodeposition from the simple salt solution. First, tin(II) ions are prone to hydrolysis. At pH higher than a certain value which is dependent on the tin(II) ion concentration (e.g. about pH 1.7 for 36 g/l stannous sulfate in our case or pH 3 for 1-2 g/l tin [50]), precipitates of colloidal hydroxide start to form in the simple salt solution. Secondly, since the hydrogen overpotential on cobalt is low, deposition of cobalt from a strong acid solution will be concurrent with strong hydrogen evolution. Since these two factors are in contradiction, in order to deposit tin-cobalt alloy, it is essential to use a complexing agent which will inhibit the hydrolysis of tin(II) and at the same time allow the pH to be adjusted to a higher value suitable for cobalt codeposition. Based on this consideration, sodium gluconate was added to the electrolyte in this research to achieve this purpose, although normally the use of a complexing agent is to bring the equilibrium electrode potential of metals closer together and thus enable alloy deposition. Of course, there are some other types of complexing agents which has been used to deposit tin-cobalt alloys, such as pyrophosphate [35], citrate [179], and heptonate [17]. However, these complex electrolytes have not attracted much attention in the past.

Gluconate forms complexes with both tin(II) and cobalt ions. In acidic media the main complex species are $[\text{SnC}_6\text{H}_{11}\text{O}_7]^+$ and $[\text{CoC}_6\text{H}_{11}\text{O}_7]^+$ [44]. As can be seen from the stability constant in Table 3.1, it is only a weak complexing agent. Despite this fact, the inhibition of tin(II) hydrolysis by the formation of gluconate complex is obvious as indicated by the increase in pH at which hydroxide precipitates form during the addition of sodium hydroxide to the electrolyte, with increase in the concentration of sodium gluconate (Figure 7.93). The more free gluconate ions, the fewer free tin(II) ions available.
for the hydrolysis reaction. The formation of a gluconate complex of cobalt(II) is also
evident as we can see from the increased polarisation after sodium gluconate was
introduced into the simple cobalt salt solution (See Figure 7.83).

With the formation of complex species, the electrode potentials of all metals are shifted to
more negative values and this often brings them closer in terms of their deposition
potential, hence producing an alloy electrodeposit. The equilibrium electrode potential of
the metal/complex ion system

\[ M^{n+} + qX^{p-} \rightleftharpoons MX_{q}^{n+pq} \]  

(7.2)
is given by the modified Nernst equation [182]:

\[ E = E^\circ - \frac{RT}{nF} \ln K + \frac{RT}{nF} \ln \frac{\alpha_{MX}^{n+pq}}{\alpha_{X^{p-}}^{q}} \]  

(7.3)

where \( q \) is the coordination number and \( X \) is the complexing ion of charge \( p \). \( K \) is the
formation constant of the complex ion and it largely determines the discharge potential of
the complexed metal ion. It has been reported that the predominant complex ions in the
sulfate/gluconate solution of pH value of about 4 are Sn(GH₄)⁺ and Co(GH₄)⁺ [44].
Substituting the values of \( E^\circ \) and \( K \) for tin and cobalt into Equation 7.3, the equilibrium
electrode potential is approximately equal to -0.225 V vs SHE for tin, and -0.294 V vs
SHE for cobalt, respectively. The difference between the equilibrium electrode potentials
becomes about 0.07 V. Therefore, apart from inhibiting tin(II) hydrolysis, gluconate does
reduce further the equilibrium potential difference between tin and cobalt.

Another advantage of using a complexing agent is that the polarisation is increased in
complexed solutions when compared to simple salt solutions. As a result, complexed
electrolytes usually have better throwing power and produce finer-grained, smoother, and
brighter deposits. Although gluconate shows no distinguishable effect on the polarisation
curves for the deposition of tin, it increases the polarisation for the deposition of cobalt
alone (Figure 7.83) or together with tin (Figure 7.84). The increased polarisation effect on
cobalt agrees well with the effect of gluconate on the deposit composition, i.e. with
increasing the quantity of sodium gluconate to the solution, the cobalt content in the
deposit decreases. However, the polarisation effect cannot explain why the deposit become
darker and even dendritic at higher concentrations of sodium gluconate. As gluconate has
negligible effect on the cathodic current efficiency (Figure 7.34), one possible reason for
this abnormal phenomenon is that with decrease in cobalt content in the deposits, the deposition of tin eventually dominates the electrocystallisation process on the electrode. In acidic electrolytes, tin deposits are prone to the formation of dendrites.

7.6.1.2 Alloy codeposition system

Brenner [181] divided all of the alloy electroplating processes into normal and abnormal codepositions. The normal codeposition is further subdivided into regular codeposition (diffusion control), irregular codeposition (activation control), and equilibrium codeposition. The characteristic of normal codeposition is that the more noble metal deposits preferentially, hence its percentage in the deposit is higher than (or equal to for equilibrium codeposition) its metal percentage in the solution. Abnormal codeposition includes anomalous codeposition and induced codeposition. In anomalous codeposition, the less noble metal, rather than the more noble one, deposits preferentially. Anomalous codeposition is rather rare and is frequently found in the electrodeposition of alloys containing one or more of the three iron-group metals: iron, cobalt, or nickel. The induced codeposition involves at least one of those metals, such as molybdenum and tungsten, which can only be deposited to form an alloy, but cannot be deposited alone.

For the electrodeposition of tin-cobalt alloys from the sulfate/gluconate bath, it is not expected to observe an anomalous codeposition behaviour as found in the deposition of zinc alloys, such as zinc-cobalt [183]. However, in the literature Sabitha et al. [34] and Sujatha et al. [35] have claimed that the deposition of tin-cobalt alloys at pH 7 and 70°C corresponds to an anomalous system as the cobalt content of the alloy obtained is always higher than that present in the electrolyte. Such an anomalous codeposition behaviour was not observed in the present experiments and cannot be interpreted using the traditional mechanism involving the formation of insoluble hydroxide films of the less noble component on the surface of the electrode [184]. In section 7.5 it has been found that only the formation of insoluble tin(II) hydroxides is possible in the sulfate/gluconate solution. Rehim et al. [67] studied the codeposition of tin-cobalt alloy from sulfate/gluconate electrolyte at pH 3.9 and room temperature. According to their results, the codeposition of tin-cobalt alloys under these conditions was classified as an irregular electroplating system. However, in the present research the electrodeposition of tin-cobalt alloys from the sulfate/gluconate system at pH 4 was found to be a regular codeposition system. The reasons are stated as follows:
First, tin is always the more noble component with comparison to cobalt in the sulfate/gluconate bath as suggested by the results of potentiodynamic polarisation studies (Section 7.4). This relative nobility between tin and cobalt is hardly affected by the variations in electroplating parameters such as the concentration of the main metal salts and the complexing agent, the addition of the surfactant, and the application of agitation. The only parameter which has significant effect on the deposition potentials for tin and cobalt is the pH value of the solution. However, as can be seen in Figures 7.78 and 7.79, even within the studied pH range from 1 to 7, the deposition potential of tin is always more positive than that for cobalt. Without any doubt tin is always more noble than cobalt in the sulfate/gluconate system under discussion, and this relative nobility is not changed by the variations of electroplating parameters.

Such observations are in agreement with the result of cyclic voltammetric studies by Gómez et al. [185] on a vitreous carbon electrode: on the negative scan the peak for the deposition of tin precedes the second peak related to the deposition of cobalt. Conversely, Rehim et al. [36] claimed that the deposition potential of tin shifts from −800 mV to −1600 mV as the concentration of stannous sulfate was varied from 20 to 2 g/l, whilst the deposition potential of cobalt (about −1200 mV) is hardly affected by change in the concentration of cobalt ions. As a result, at high concentrations of tin(II) ions tin is the more noble component, whereas at low tin(II) ion concentrations, cobalt becomes the more noble component. However, this statement is in doubt after a perusal of the corresponding polarisation curves. The significant change observed on their polarisation curves is actually the difference in the polarisation behaviours for the deposition of tin and the evolution of hydrogen, rather than that for the deposition of tin alone, which was not revealed clearly due to the low concentration of stannous sulfate, e.g. 2 g/l, used in their investigation.

Secondly, the more noble component, tin, is always deposited preferentially. At low current densities, tin deposits in a pure, unalloyed state. This is evidenced by the relationship between deposit composition and the applied current density in Figure 7.4 and also the results of Hull cell tests in Figures 7.22-7.24. The off-white zones at the low current density end of the Hull cell test panels correspond to deposits of pure tin. The less noble cobalt begins to codeposit only after the limiting current density for the deposition of tin has been exceeded and with further increase in current density, the cobalt content in the deposit increases. Under such conditions, the deposition of tin is under diffusion control
whilst the deposition of cobalt is under activation or mixed (diffusion and activation) control. As the current density is increased even further so that both tin and cobalt are deposited at their own limiting current densities, the cobalt content in the deposit finally approaches a value controlled by the cobalt content in the electrolyte. Such kind of variation of deposit composition with the current density is a typical behaviour of a regular codeposition system [181].

Finally, for a regular codeposition system, one special and easily recognisable characteristic is that the effects of electroplating variables on the deposit composition are consistent and predictable from simple diffusion theory. As the more noble component in a regular alloy codeposition system is deposited at its limiting current density $j_{lim}$, which, according to Fick’s first law of diffusion, and from a solution with the addition of inert conductive salts is:

$$ j_{lim} = \frac{nFDC_b}{\delta} $$

(7.4)

any parameters which increase the limiting current density for deposition of the more noble metal will increase its content in the electrodeposited alloy. From equation 7.4, it is obvious that the increase in the magnitude of the following electroplating variables will lead to an increased content of the more noble metal in the alloy deposit:

- Agitation of the electrolyte, which increases the limiting current density by reducing the diffusion layer thickness $\delta$;
- Total metal concentration of the bath (ratio of the main metal ions being kept constant), which increases the concentration of metal ions in the bulk solution $C_b$;
- Ratio of the more noble metal ions to the less noble metal ions (keeping constant the total metal concentration of the bath);
- Temperature of the electrolyte, which increases the diffusion rate of metal ions to the cathode as reflected by an increased diffusion coefficient.

However, the content of the more noble metal in the alloy deposit decreases with increase in the total applied current density, since more current, which is the excess of current above that required to deposit the more noble metal at its limiting rate, becomes available for the deposition of the less noble metal (and also for the evolution of hydrogen when the current efficiency is not 100%).
For the present tin-cobalt alloys, it can be seen in Section 7.1 that the effects of electroplating variables on the related electrodeposition process from a sulfate/gluconate bath at pH 4 actually conform to all of the above-mentioned regularities for a regular alloy codeposition system. The deposition of the more noble component, tin, is favoured remarkably by stirring the electrolyte (Figure 7.11) and increasing the concentration of tin(II) ions in the bulk solution (Figure 7.8), or to a less extent by raising the temperature of the electrolyte (Figure 7.13). However, the deposition of the less noble component, cobalt, is enhanced by increasing the current density (Figure 7.4).

For all these reasons, it may be concluded that the electrodeposition of tin-cobalt alloy from a sulfate/gluconate bath at pH 4 forms a regular codeposition system. Nevertheless, it is worth noting that on those curves showing the relationship between the deposit composition and the current density obtained from the initial solution which contained 12 g/l stannous sulfate and 8 g/l cobalt sulfate, there exists a maximum at a current density of around 1-2 A/dm² (Figure 7.4). The cobalt content in the deposit decreases with further increase in the applied current density after it attains the cobalt metal percentage in the solution. This phenomenon is not contrary to the effect of current density on a regular codeposition system. It can be explained by the increasing effect of agitation on the limiting current density of tin due to the evolution of hydrogen at high current densities. The agitation produced by the bubbles of hydrogen increases the convection and thus decreases the diffusion layer thickness, which leads to an increase of the limiting current density of metal deposition. It has experimentally shown that the evolution of hydrogen can double the limiting current density [181]. As a result of enhanced deposition of tin, the cobalt content in the alloy deposit decreases. According to this explanation, the deposit composition at high current densities should be more stable in a well-agitated solution, since the diffusion layer thickness is less affected by the evolution of hydrogen. This speculation is confirmed by the result obtained in the investigation on the effect of agitation (Figures 7.11-7.12). On the other hand, this decrease in cobalt content in the deposits may also be a result of the formation of insoluble tin(II) hydroxide films on the surface of the cathode, which impedes the deposition rate of cobalt.
7.6.2 Effect of pulse electroplating parameters

In Section 7.2 it was demonstrated that apart from its effect on the deposit morphology, pulsed current also exhibits marked influence on the cobalt content in tin-cobalt alloys. According to Landolt *et al.* [186], the extent to which pulse parameters can influence the alloy composition depends on the kinetics of the partial reactions. For the codeposition of two components which are under charge transfer control, pulse electroplating is only expected to have some effects on the alloy composition if the partial reduction reactions have different Tafel slopes. In contrast, strong dependence of alloy composition on pulse parameters could be found in the codeposition of two components when the more noble component is under mass transport control and the other is under charge transfer control. For the electrodeposition of tin-cobalt alloys, it corresponds to the latter case, as discussed in Section 7.6.1. On this basis, it is not surprising that pulse electroplating parameters have appreciable effects on the composition of tin-cobalt alloys, but more efforts should be made on understanding these effects. In the following sections, the mechanism by which pulse parameters affect the composition of tin-cobalt alloys will be discussed in terms of the following characteristics of pulse electroplating:

- Capacitance effects of the electrical double layer
- Displacement reaction during the off-time
- Mass transport effect

7.6.2.1 Capacitance effects

For pulse electroplating, one of the conditions which is different from that in direct current electroplating is that the electrical double layer at the electrode/solution interface, which behaves like a parallel plate capacitor, has to be repeatedly charged and discharged as the applied current is abruptly switched on and off periodically. According to Puippe [66], capacitance effects of the electrical double layer may lead to the flattening of the faradaic current for metal deposition, if the on-time of the pulsed current is shorter than the charging time $t_c$ of the electrical double layer. In extreme cases when both the on-time and the off-time are shorter than the charging time $t_c$ and the discharging time $t_d$, respectively, the expected pulse electroplating will virtually approach the condition of a direct current. The corresponding faradaic current density only oscillates around the average current

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density. Normally, the pulse electroplating parameters in most studies are designed so that the capacitance effects can be neglected. However, in this research it might be necessary to take into consideration the capacitance effect on the variation of tin-cobalt alloy composition with the pulse parameters. The reason is that the peak current density was varied within a wide range starting from less than 1 A/dm\(^2\). At such small peak current densities, the charging time and the discharging time are relatively long and may not be negligible any more for high pulse frequencies, such as 500 Hz for the duty cycle of 50%.

The damping of the faradaic current has been found to affect the nucleation rate and the current distribution [66], but no report can be found on its related effects on the composition of alloy deposits. For a regular codeposition system like tin-cobalt alloy codeposition, it is reasonable to expect that the capacitance effect will lead to an increase of the more noble component in the deposit as a result of the decreased pulse amplitude of the faradaic current density for metal deposition.

For the evaluation of capacitance effects in pulse electroplating of tin-cobalt alloys, equation 4.13 is employed to estimate the order of magnitude of \( t_c \) since the electrical parameters for the accurate calculation of this parameter, such as the exchange current density and the capacitance of the electrical double layer are not readily available. For a given waveform with a duty cycle \( \theta \), the frequency corresponding to the on-time equal to the charging time is

\[
f = \frac{\theta}{t_{on}} = \frac{\theta}{t_c}
\]

(7.5)

Converting the unit of current density \( j_p \) in equation 4.13 from A/cm\(^2\) to A/dm\(^2\) and the unit of \( t_c \) from microsecond to second, and then substituting \( t_c \) into equation 7.5 yields

\[
f = \frac{j_p \theta}{1.7} \times 10^3 = \frac{j_n}{1.7} \times 10^3 \text{ Hz}
\]

(7.6)

Equation 7.6 gives the minimum frequency \( f_{\text{min}} \) for the capacitance effect. Any pulsed current of a frequency higher than \( f_{\text{min}} \) will lead to the capacitance effect being experienced. Table 7.21 gives the calculated values of the minimum frequency \( f_{\text{min}} \) at different average current densities.
Table 7.21 Estimation of the minimum frequency for capacitance effects at different average current densities

<table>
<thead>
<tr>
<th>( j_m ) A/dm(^2)</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_{\text{min}} ) Hz</td>
<td>294</td>
<td>588</td>
<td>1176</td>
<td>1765</td>
<td>2353</td>
<td>2941</td>
</tr>
</tbody>
</table>

Table 7.22 Maximum frequency applied for pulsed current waveforms with different duty cycles

<table>
<thead>
<tr>
<th>( \theta ) %</th>
<th>90</th>
<th>80</th>
<th>66</th>
<th>50</th>
<th>33</th>
<th>20</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_{\text{max}} ) Hz</td>
<td>100</td>
<td>200</td>
<td>333</td>
<td>500</td>
<td>333</td>
<td>200</td>
<td>100</td>
</tr>
</tbody>
</table>

Comparing the minimum frequency for capacitance effects in Table 7.21 with the maximum applied frequency in Table 7.22, which was limited by the shortest time interval of 1 millisecond of the pulse generator, it was found that capacitance effects are not relevant at average current densities higher than 1 A/dm\(^2\) for any pulsed current waveforms, since the corresponding minimum frequency required for effective capacitance effects is always higher than all of the maximum applied frequencies. Therefore, the decrease in the cobalt content with the frequency in Figure 7.25 could not be interpreted by the capacitance effect. At average current densities lower than 1 A/dm\(^2\), however, the capacitance effect might have to be taken into consideration as the minimum frequency for capacitance effects may be lower than the applied frequency depending on the duty cycle.

Note that the evaluation of the capacitance effect described above must be taken with caution as its reliability depends on the validity of Equation 4.13, which was derived from the assumption that the peak current density \( j_p \) is more than 100 times higher than the exchange current density \( j_o \), \( j_p/j_o > 100 \), and the capacitance is 50 \( \mu \text{F/cm}^2 \). For small \( j_p \) values, e.g. \( j_p/j_o < 100 \), Equation 4.13 will no longer hold and will produce overestimated values of charging time [66]. Similarly, if the actual capacitance of the system of study is lower than 50 \( \mu \text{F/cm}^2 \), Equation 4.13 could also produce overestimated values.
7.6.2.2 Displacement reactions during the off-time

As the capacitance effect alone cannot explain the composition variations under all of the experimental conditions in this research, it is necessary to look further into other possible mechanisms. In the literature it was found that another factor which may contribute to the effect of pulse electroplating parameters on alloy composition is the displacement reaction during the off-time [187-189]. Due to the difference in nobleness of alloy components, the less noble metal can be selectively dissolved or displaced from the alloy by the more noble one at the rest potential. It has been found that for certain alloy systems like Ni-Cu [187] and Co-Cu [189] alloys, displacement reaction during the off-time has significant influence on the alloy composition.

Like selective dissolution of the less noble component in alloys such as α-brass [190], Cu-Pd and Ag-Au [191] in aqueous solution, the displacement reaction during the off-time manifests itself by a surface layer enriched in the more noble component and depleted in the less noble component. Auger electron spectroscopy (AES) analysis [187] has been used as an ex situ method to detect such surface layers. As to the rate of the displacement reaction during the off-time, it may vary with time. Initially, the normal electrochemical kinetics apply and the slowest step, either the mass transport of ion species in the electrolyte [187, 189] or the charge transfer on the electrode, control the reaction rate. With the progress of the reaction and the increasing surface coverage by the more noble component, the concentration of less noble component at the surface decreases. To maintain the reaction the less noble component has to be transported from the bulk alloy to the surface by volume diffusion. The displacement reaction, therefore, is progressively suppressed and the reaction rate decreases with time to very small values. Under such conditions, the solid state diffusion becomes the rate controlling process.

To find out if a displacement reaction was present during the off-time in pulse electroplating of tin-cobalt alloys, AES analysis was conducted with two samples about 1 micron thick, prepared at the current density of 2 A/dm² by direct current. One sample was removed from the solution immediately after deposition. The other was immersed in the solution after deposition for another 30 minutes before being removed from the solution. The elements detected and the corresponding contents are shown in Tables 7.23 and 7.24. The depth profiles for tin, cobalt, and oxygen are shown in Figure 7.94. Apparently, there is no enrichment of tin, the more noble component, in tin-cobalt alloys on the surface of
the deposit which was immersed in the solution for 30 minutes. On the contrary, there is a layer (about 12 nm) in which no cobalt is detected on the surface of the deposit removed from the solution immediately. Except for this, there is no significant difference in the tin and cobalt profiles. The concentrations of tin and cobalt in the two deposits have almost the same values in the bulk alloy and approaching the surface, both of them decrease rapidly. If there were a displacement reaction, an increased concentration profile of tin at the surface would be expected. Therefore, AES depth profiling did not support the presence of a displacement reaction during the off-time for the deposition of tin-cobalt alloys.

Table 7.23 AES data of the composition (atom%) for the deposit removed from the solution immediately after the electroplating. (excluding H, He)

<table>
<thead>
<tr>
<th>Etch time s</th>
<th>Depth nm</th>
<th>P</th>
<th>Cl</th>
<th>C</th>
<th>Sn</th>
<th>O</th>
<th>Co</th>
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<td>25.7</td>
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<td>56.3</td>
<td>38.7</td>
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<td>0.0</td>
<td>71.0</td>
<td>29.0</td>
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</tr>
<tr>
<td>120</td>
<td>24</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>72.3</td>
<td>24.0</td>
<td>3.7</td>
</tr>
<tr>
<td>300</td>
<td>60</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<td>8.2</td>
</tr>
<tr>
<td>900</td>
<td>180</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>79.1</td>
<td>8.0</td>
<td>12.9</td>
</tr>
<tr>
<td>1500</td>
<td>300</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>73.9</td>
<td>9.2</td>
<td>16.9</td>
</tr>
</tbody>
</table>

Table 7.24 AES data of the composition (atom%) for the deposit immersed in the solution for another 30 minutes after the electroplating. (excluding H, He)

<table>
<thead>
<tr>
<th>Etch time s</th>
<th>Depth nm</th>
<th>P</th>
<th>Cl</th>
<th>C</th>
<th>Sn</th>
<th>O</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>3.7</td>
<td>11.1</td>
<td>33.9</td>
<td>47.1</td>
<td>4.2</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>0.0</td>
<td>2.1</td>
<td>0.0</td>
<td>51.5</td>
<td>38.5</td>
<td>7.9</td>
</tr>
<tr>
<td>600</td>
<td>120</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>62.6</td>
<td>23.0</td>
<td>14.4</td>
</tr>
<tr>
<td>1500</td>
<td>300</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>81.8</td>
<td>2.0</td>
<td>16.2</td>
</tr>
</tbody>
</table>
The data in Tables 7.23 and 7.24 also indicates no carbon in the bulk of the tin-cobalt alloy deposit. This observation is of interest because it may imply that there is no inclusion of organic materials from the electrolyte, such as the non-ionic surfactant Tween 20, which was believed to function by virtue of adsorption on the electrode surface. This result may also suggest that the non-ionic surfactant either does not undergo any reduction reaction on the cathode, or its reduction products enter the solution instead of being adsorbed on the cathode surface. The phosphorus and chlorine detected at the surface could be due to impurities in the electrolyte.

A displacement reaction during the pulse off-time is not a necessity. It has been verified experimentally that there was no such reactions taking place during the pulse electroplating of Ni-Mo alloys [192]. Therefore, the absence of a displacement reaction during the off-time in the deposition of tin-cobalt alloys is also reasonable. First, for the displacement reaction to take place, the driving force, the difference between the equilibrium electrode potentials of the two constituent metals in the electrolyte, should be sufficiently large. As we already discussed in Section 7.6.1.1, the difference between the equilibrium electrode potentials of tin and cobalt in the sulfate/gluconate electrolyte is approximately 0.07 V. With such a small potential difference, the displacement reaction, if possible, could not proceed at an appreciable rate.

Secondly, it is well known from corrosion studies that selective dissolution of the less noble component usually occurs in single-phase alloys forming solid solutions or in alloys with constituents which are totally immiscible [191]. According to the thermal phase diagram of tin-cobalt alloy system [54], tin and cobalt only have very low mutual solid solubility for each other at room temperature and they form intermetallic compounds such as tetragonal CoSn₂ (20% Co), hexagonal CoSn (33.3% Co), and possibly hexagonal γ/Co₃Sn₂ (about 41% Co). Considering there may exist some difference between the structures of the electrodeposited and thermally prepared alloys, X-ray diffraction was conducted to identify the phases that existed in tin-cobalt alloy deposits. Figure 7.95 shows the X-ray diffraction patterns of the electrodeposited tin and tin-cobalt alloy deposits by both direct and pulsed current. It shows narrow peaks indicating well crystallised phases in the deposits. Besides those peaks corresponding to the tin phase, there were some peaks left which cannot be indexed as any of the phases in the thermal phase diagram of the tin-cobalt system. Similar results have also been obtained by other researchers [34] and they
ascribed these peaks to a new tetragonal CoSn phase which does not exist in thermally prepared tin-cobalt alloys. There is no indication that tin and cobalt can form solid solution phases. Therefore, from the viewpoint of deposit structure, the displacement reaction is not likely to take place in tin-cobalt alloys.

Finally, the selective dissolution of the less noble component requires a minimum content of it in the alloy. It has been established in the corrosion study of binary alloys that the dissolution mode could exhibit a transition from selective dissolution of the less noble content to simultaneous dissolution of both components depending on the alloy composition. For example, the transition occurs if there is less than 90% Cu for Cu-Pd alloys, less than 90% Ni for Ni-Pd alloys, and less than 80% Ag for Ag-Au alloys [191]. For Cu-Zn alloys, as zinc is very active, selective dissolution of zinc could take place even in the alloy with 30% zinc [190]. The increase in noble metal content raises the overpotential for selective dissolution of the less noble component and thus suppresses the selectivity. For tin-cobalt alloys in this research, the content of the less noble component, cobalt, is normally not more than 20%. Considering the position of cobalt in the electrochemical series, such a content might not be sufficient to favour its selective dissolution.

7.6.2.3 Mass transport effect

With the ruling out of the presence of a displacement reaction during the off-time, the most likely pulse parameter which affects the composition of tin-cobalt alloy deposits should be the non-steady state mass transport in pulse electroplating. In the literature, both the analytical [79] and numerical solutions [80] are available with respect to the mass transport of the reacting species towards the cathode during pulse electroplating with square current waveforms as shown in Figure 4.2(a). In contrast to the complicated mathematics involved in solving the differential diffusion equation in order to obtain the analytical or numerical solutions, Ibl [74], introduced the concept of a pulsating diffusion layer and proposed a duplex linear diffusion layer model. This simplified model provides an essentially correct physical insight into the mass transport phenomena during pulse electroplating. However, no detailed derivation of those equations in Ibl's model was published in English language journals [74]. Therefore, the understanding and application of this model were sometimes found difficult. In the following sections, those equations will derived in a different way
and the result will be used to interpret the effect of pulse parameters on the deposition of tin-cobalt alloys.

7.6.2.3.1 Theoretical consideration

In reference 74, IbI started the mathematical description of the duplex diffusion layer from the first pulse. Here only the situation after the quasi-stationary state of the diffusion layer has been attained (Figure 7.96) will be considered. Under such a circumstance, the concentration profile (line NP) within the stationary diffusion layer will not change with time and will have a constant concentration gradient by which the reacting species is transported from the bulk solution to the pulsating diffusion layer. Within the pulsating diffusion layer, the concentration profile starts from the horizontal line PS₁ and develops into PS₂ during the on-time and then is restored from PS₂ to the original position PS₁ during the off-time.

Consider the material balance in the whole diffusion layer, namely the section from x = 0 to x = δₙ (as shown in Figure 7.96). Assume at x = 0, the reacting species is removed (due to deposition reaction) from the section at a rate of J₁, whilst at x = δₙ the reacting species is replenished into the section by diffusion at a rate of J₂.

\[
J_1 = \frac{J_p}{nF} \tag{7.7}
\]

\[
J_2 = D \left( \frac{\partial C}{\partial x} \right)_{x=\delta_n} \tag{7.8}
\]

After one pulse, the concentration profile in the whole diffusion layer will shift from line NPS₁ to NPS₂. The corresponding mass change ΔM₁ (< 0) in the diffusion layer is:

\[
\Delta M_1 = J_2 t_{on} - J_1 t_{on} \tag{7.9}
\]

After one pause, the concentration is then restored from NPS₂ to NPS₁ resulting in a mass change ΔM₂ (> 0) in the diffusion layer. As J₁ during the off-time is zero,

\[
\Delta M_2 = J_2 t_{off} - J_1 t_{off} = J_2 t_{off} \tag{7.10}
\]

ΔM₁ and ΔM₂ are equal in size (represented by the grey area ΔM) but opposite in sign, so

\[
\Delta M_1 + \Delta M_2 = J_2 t_{on} - J_1 t_{on} + J_2 t_{off} = 0 \tag{7.11}
\]

Rearranging Equation 7.11 and substituting Equation 7.7 into it, this yields

\[
J_2 = J_1 \frac{t_{on}}{t_{on} + t_{off}} = J_1 \theta = \frac{j_p \theta}{nF} = \frac{j_m}{nF} \tag{7.12}
\]
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From Equations 7.8 and 7.12, one obtains

\[
D \left( \frac{\partial C}{\partial x} \right)_{x=\delta_N} = \frac{j_m}{nF} \tag{7.13}
\]

Equation 7.13 is important, as it proves that the concentration gradient at \( x = \delta_N \) corresponds to that under dc electrolysis at the average current density. For the linear approximation of the diffusion layer, the slope of the concentration profile \( NP \), which from Figure 7.96 can be expressed as \( \frac{C_0 - C_{s1}}{\delta_N - \delta_P} \), is constant everywhere in the stationary diffusion layer. Therefore the slope of line \( NP \) can be related to the average current density as

\[
\text{Slope of line } PN = \frac{C_0 - C_{s1}}{\delta_N - \delta_P} = \left( \frac{\partial C}{\partial x} \right)_{x=\delta_N} = \frac{j_m}{nFD} \tag{7.14}
\]

Since diffusion is assumed as the only mechanism of mass transport in the whole diffusion layer, the deposition rate and the diffusion rate of the reacting species at the cathode (\( x=0 \)) must be equal. This yields,

\[
J_i = \frac{j_p}{nF} = D \left( \frac{\partial C}{\partial x} \right)_{x=0} \tag{7.15}
\]

Also as a result of the linear approximation of the concentration profile in the pulsating diffusion layer, the slope of line \( PS_2 \) is related to the peak current density by

\[
\text{Slope of line } PS_2 = \frac{C_{s1} - C_{s2}}{\delta_P} = \left( \frac{\partial C}{\partial x} \right)_{x=0} = \frac{j_p}{nFD} \tag{7.16}
\]

To determine the thickness of the pulsating diffusion layer \( \delta_P \), the mass change \( \Delta M_1 \) after a pulse is reconsidered. Substituting Equations 7.7 and 7.12 into Equation 7.9, one obtains

\[
\Delta M_1 = \frac{(j_m - j_p)}{nF} t_{on} = -\frac{j_p (1 - \theta)}{nF} t_{on} \tag{7.17}
\]

\[
= -D \frac{(C_{s1} - C_{s2})}{\delta_P} (1 - \theta) t_{on}
\]

on the other hand, \( \Delta M_1 \) can also be calculated by the integration of the concentration profiles along \( x \), which yields

\[
\Delta M_1 = -\Delta M = -\frac{(C_{s1} - C_{s2})\delta_P}{2} \tag{7.18}
\]

Combining Equations 7.17 and 7.18 and after rearranging, one obtains
\[ \delta_p = \sqrt{2Dt_{\text{on}}(1-\theta)} \quad (7.19) \]

With the knowledge of pulsating diffusion layer thickness \( \delta_p \), the surface concentration values \( C_{so}, C_{s1}, C_{s2} \) can be determined as follows. From Figure 7.96,

\[ C_{so} = C_0 - (C_0 - C_{so}) = C_0 - \frac{J_{p\text{n}}}{nFD} \delta_n \quad (7.20) \]

Rearranging Equation 7.14, one obtains

\[ C_{s1} = C_0 - \frac{J_{n}}{nFD} (\delta_n - \delta_p) = C_{so} + \frac{J_{p\text{n}}}{nFD} \delta_p \quad (7.21) \]

Combining Equations 7.16 and 7.21 and after rearranging,

\[ C_{s2} = C_{s1} - \frac{J_{p\text{n}}}{nFD} \delta_p = C_{so} - \frac{J_{p\text{n}}(1-\theta)}{nFD} \delta_p \quad (7.22) \]

For pulse electroplating with fixed on-time and off-time but variable peak current density, there is a characteristic current density, which is the pulse limiting current density \( I_{\text{pl}} \). As defined by Cheh [80], \( I_{\text{pl}} \) is the peak current density which causes the surface concentration \( C_{s2} \) at the end of a pulse to reach zero. Letting \( C_{s2} = 0 \), Equation 7.22 yields

\[ C_{so} = \frac{J_{p\text{n}}(1-\theta)}{nFD} \delta_p \quad (7.23) \]

Introducing the limiting current density \( J_{\text{lim}} \) under direct current conditions, we can write

\[ \frac{J_{\text{lim}}}{nF} = D \frac{C_0}{\delta_n} \quad (7.24) \]

Rearranging Equation 7.24 and substituting the expression for \( C_0 \) into Equation 7.20, we have

\[ C_{so} = \frac{J_{\text{lim}} - J_{p\text{n}}}{nFD} \delta_n \quad (7.25) \]

Combining Equations 7.23 and 7.25 and rearranging, the pulse limiting current density is related to the dc limiting current density as

\[ \frac{J_{\text{lim}} - J_{p\text{n}}}{J_{p\text{n}}(1-\theta)} = \frac{\delta_p}{\delta_n} \quad (7.26) \]

On the other hand, for pulse electroplating with a constant peak current density, there is a characteristic on-time, namely, the transition time \( \tau \). When the on-time is equal to the
transition time, the concentration of the reacting species at the electrode surface drops to zero. Setting $C_{s2} = 0$ in Equation 7.22 and substituting $t_{on}$ for $\delta_p$ according to Equation 7.19, we obtain the transition time

$$\tau = \frac{D}{2 (1 - \theta)^3} \left( \frac{nFC_{s0}}{j_p} \right)^2$$

(7.27)

As $C_{s0} = (1 - \theta)C_{s1}$ when $C_{s2} = 0$ (from Equations 7.21 and 7.22), Equation 7.27 can also be written as

$$\tau = \frac{D}{2 (1 - \theta)^3} \left( \frac{nFC_{s1}}{j_p} \right)^2$$

(7.28)

However, in Ibl's original derivation [74] the transition time was given as

$$\tau = \frac{D}{2} \left( \frac{nFC_0}{j_p} \right)^2$$

(7.29)

which was later corrected to Equation 7.30 without any explanation

$$\tau = \frac{D}{2} \left( \frac{nFC_{s1}}{j_p} \right)^2$$

(7.30)

Apparently, Equation 7.29 is only applicable for the situation when at the end of the first pulse the interface concentration drops to zero. Under the conditions given by Equation 7.29, during the following cycles the interface concentration drops to zero before the end of the on-time. Therefore, the consequent transition time from Equation 7.29 is of no significance in pulse electroplating. Equation 7.30 differs from Equation 7.28 by $1/(1-\theta)$. It only holds when the duty cycle is very small and thus negligible. Equation 7.27 (or 7.28) considers the situation when the quasi-stationary state of the mass transport has arrived, namely the concentration profile of the reacting species will fluctuate between two fixed positions. Equation 7.27 or 7.28, rather than Equation 7.29, gives a more reasonable description of the transition time and they should be used in the future calculations. As it is not convenient to deal with $C_{s0}$, Equation 7.27 needs further modifications. Substituting Equation 7.25 for $C_{s0}$ into Equation 7.27, we obtain

$$\tau = \frac{\delta_N^2}{2D(1-\theta)^3} \left( \frac{i_{lim}}{j_p} - \theta \right)^2$$

(7.31)

Once the parameters $\delta_N$, $D$, $i_{lim}$, are known for a system with well-defined hydrodynamic conditions, the transition time can then be calculated by Equation 7.31 for a waveform with a constant peak current density and duty cycle. Introducing the dimensionless transition
time $\tau^* = \frac{D\pi}{\delta_N^2}$ and the dimensionless peak current density $i_p^* = \frac{j_p}{j_{lim}}$ (so that the equation can be simplified and plotted without knowing some parameters, e.g. $D$ and $\delta_N$ for a specific system), one gets

$$\tau^* = \frac{1}{2(1-\theta)^3} \left( \frac{1}{j_p^*} - \theta \right)^2$$  \hspace{1cm} (7.32)

This relationship is plotted in Figure 7.97. For the purpose of comparison, the dimensionless transition time for a single galvanostatic pulse (or for a direct current condition) is also plotted according to the Equation 7.33 [66]

$$\tau^* = \frac{\pi}{4j_p^2} \text{ for } \tau^* < 0.1$$ \hspace{1cm} (7.33 a)

$$\tau^* = -\frac{4}{\pi^2} \ln \left[ \frac{\pi^2}{8} \left( 1 - \frac{1}{j_p^2} \right) \right] \text{ for } \tau^* > 0.1$$ \hspace{1cm} (7.33 b)

The transition time for pulsed current shows a strong dependence on both the duty cycle and the peak current density. With comparison to a single galvanostatic pulse, a large discrepancy between their transition times exists when the duty cycle of the pulsed current is high, e.g. 50%. For small duty cycles, the transition time for a pulsed current is always shorter than that for a single galvanostatic pulse and part of the curve for the pulsed current is parallel to that for the single galvanostatic pulse under certain conditions, which simplify Equation 7.32 to

$$\tau^* = \frac{1}{2j_p^2} \text{ for } \theta << 1 \text{ and } \frac{1}{j_p^*} >> \theta$$ \hspace{1cm} (7.34)

Equation 7.33a and Equation 7.34 show the same dependence of the dimensionless transition time on the dimensionless peak current density and only differ in the numerical coefficient. Landolt [185] claimed that the disagreement between Equation 7.33a and 7.34 was a disadvantage and could be avoided by making some correction for the pulsating diffusion layer thickness $\delta p$. However, this correction needs to be treated with caution as it might lead to overestimated transition times when the condition $\frac{1}{j_p^*} >> \theta$ is not valid, namely when the applied current is sufficiently high (correspondingly the average current density is high). The reason is that the error due to the linear approximation in Ibl's duplex diffusion layer model becomes smaller with decrease in the pulsating diffusion layer.
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This implies that the small transition time (i.e., small δp according to Equation 7.19) from Equation 7.32 at sufficiently high peak current densities is closer to the true value and, therefore, needs no correction.

7.6.2.3.2 Maximum rate of metal deposition

In the Section 7.6.2.3.1, the pulse limiting current density (Equation 7.26) was defined. However, it must be noted that this limiting current density is by no means the maximum rate of metal deposition as has been pointed out by Puippe [66]. The pulse limiting current density is only the maximum peak current density at which the current efficiency for metal deposition is still 100%. For alloy electrodeposition the pulse limiting current density is, therefore, the maximum peak current density at which the more noble component can still be deposited in an unalloyed state. Figure 7.98 illustrates the variation of the actual metal deposition rate with time during the on-time when the applied peak current density is higher than the pulse limiting current density. It was assumed that the pulsed current has fixed on-time and off-time (this means constant duty cycle and frequency) and the peak current density is the only variable. As can be seen from Figure 7.98, the actual metal deposition rate can be maintained equal to the applied peak current density up to the corresponding transition time only. After that the actual metal deposition rate decreases gradually and may eventually reach the dc limiting current density \( j_{\text{lim}} \) at the end of on-time depending on circumstances. The reason for the decrease in the actual metal deposition rate during \( t > \tau \) is that the concentration of the reacting species at the electrode surface drops to zero at \( t = \tau \) and the subsequent metal deposition switches from deposition at a constant rate to deposition with constant surface concentration of zero. The concentration gradient at the electrode surface then decreases with time since for \( t > \tau \), the surface concentration cannot drop further. In spite of the decrease in the metal deposition rate during the interval from \( \tau \) to \( t_{\text{on}} \), the total metal deposited during the on-time, \( \int_{t_{\text{on}}}^{t_{\text{off}}} j_p(t)dt \), which is represented by the area under the curve for the actual deposition rate \( j_p(t) \), increases with increasing applied peak current density. Therefore, the average peak current density \( \bar{j}_p = \frac{1}{t_{\text{on}}} \int_{t_{\text{on}}}^{t_{\text{off}}} j_p(t)dt \) during the on-time (and accordingly the actual average current density \( j_m = j_p \theta \)) for metal deposition increases with increase in the applied peak current density \( j_p \).
The variation of the total average current density \( j_m \), and the actual average current density for metal deposition \( \bar{j}_m \), with the applied peak current density \( j_p \) is further illustrated in Figure 7.99. Since \( j_m = j_p \theta \) always holds, this relation is represented as a straight line with a slope equal to the duty cycle \( \theta \). The actual average current density corresponding to an applied peak current density \( j_p \) at a certain frequency is represented as the pink line. Apparently, \( \bar{j}_m = j_m = j_p \theta \) (so \( \bar{j}_p = j_p \)) is valid until \( j_p = j_{PL} \). Beyond \( j_{PL} \), \( \bar{j}_m < j_m \) but \( \bar{j}_m \) still increases with \( j_p \) until it reaches the dc limiting current density for the metal \( (\bar{j}_m = \bar{j}_{lim}) \). Using Figure 7.99, it is also very easy to define the average peak current density \( \bar{j}_p \), such as \( \bar{j}_{PL} \) corresponding to the applied peak current density \( j_p \) and the actual average current density \( \bar{j}_m \) in the figure (due to \( \bar{j}_m = \bar{j}_{PL} \theta \)). Finally, Figure 7.99 also indicates that no matter how high the applied peak current density may be, the maximum average deposition rate \( (\bar{j}_m)_{\text{max}} \) for a metal could never exceed its dc limiting current density and thus the maximum average peak current density \( (\bar{j}_p)_{\text{max}} \) could never exceed \( \frac{\bar{j}_{lim}}{\theta} \), namely

\[ 0 \leq \bar{j}_m \leq \bar{j}_{lim} \]  
\[ 0 \leq \bar{j}_p \leq \frac{\bar{j}_{lim}}{\theta} \]  

In Figure 7.99 we have only considered the variation of the deposition rate with the applied current density at one specified frequency. For a current waveform with a fixed duty cycle, the frequency, like the applied peak current density, could also be varied within a very wide range. The effect of frequency on the relationship between the actual average current density and the applied peak current density is illustrated in Figure 7.100. With increase in the frequency from very low \( (f_o) \) to very high \( (f_m) \), the pulse limiting current density \( j_{PL} \) increases from \( j_{lim} \) to \( \frac{\bar{j}_{lim}}{\theta} \). This trend is predicted on the basis of Equation 7.26. When the frequency is very low, \( \delta_p \rightarrow \delta_N \). From Equation 7.26, we have \( j_{PL} \rightarrow j_{lim} \). Similarly, when the frequency is very high, \( \delta_p \rightarrow 0 \) and therefore \( j_{PL} \rightarrow \frac{\bar{j}_{lim}}{\theta} \). At very low frequencies, since the on-times are so long that the corresponding pulse electroplating is virtually a direct current one and during most of the on-time the actual peak current density
for metal deposition is the limiting current density (after \( j_p > j_{\text{lim}} \)). This leads to an average current density for metal deposition not dependent on the applied peak current density, which is reflected as a horizontal line on Figure 7.100 corresponding to very low frequencies. On the other hand, it is necessary to emphasise that for any current waveform with a fixed duty cycle, the pulse limiting current density could never exceed \( \frac{j_{\text{lim}}}{\theta} \) no matter how high the frequency is. Very high pulse limiting current density is only obtainable with very small duty cycles.

### 7.6.2.3.3 Current density range for pure tin

The deposition characteristics of tin-cobalt alloys under pulsed current conditions were presented in Section 7.4.2. The results can now be explained by the mass transport theory of pulse electroplating described in the last two sections. Before the detailed discussion on the effects of pulse parameters on tin-cobalt alloy composition, the relationship between the cobalt content in the deposits and the applied current density is needed. It has been established in Section 7.6.1.2 that the electrodeposition of tin-cobalt alloys from the sulfate/gluconate electrolyte forms a regular codeposition system and the deposition of tin is always preferred. This characteristic enables the alloy composition to be predicted according to the equations in Table 7.25.

As can be seen from Figures 7.18, and 7.26-29, for any of the current waveforms with a fixed duty cycle and frequency, there always exists a current density range at the lower end, within which only pure tin was deposited. The width of this current density range was of interest because for the future electrodeposition of compositionally modulated tin-cobalt alloy multilayer coatings a wide operation window for the deposition of pure tin sublayers was needed as shown in Figure 6.1.

According to Equation 7.37, the upper limit of the current density range where only pure tin was deposited corresponds to the limiting current density of tin under DC conditions, or the pulse limiting current density under PC conditions. As described in Section 7.6.2.3.2 for any frequency the pulse limiting current of tin, \( j_{pL,Sn} \), always falls in the following range

\[
 j_{\text{lim},Sn} \leq j_{pL,Sn} \leq \frac{j_{\text{lim},Sn}}{\theta}
\] (7.40)
Therefore, from Equation 7.40 the curves of the cobalt content in the deposits plotted against the peak current density for pulse electroplating should always stand at the right hand side of the curve for direct current electroplating. This trend was confirmed in Figures 7.26(a) and 7.28. In Figure 7.26(b), the curves for the on-time from 20 to 90 ms stands on the left of the curve for direct current electroplating. Therefore there must exist some experimental errors on the deposit composition on those curves.

**Table 7.25** Dependence of cobalt content in the deposits on the applied current density under both direct current (DC) and pulsed current (PC) conditions

<table>
<thead>
<tr>
<th>Applied current density</th>
<th>Alloy composition</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j \leq j_{\text{lim,Sn}}$</td>
<td>$X_{Co} = 0$</td>
<td>7.37 (a)</td>
</tr>
<tr>
<td>$j_{\text{lim,Sn}} &lt; j \varepsilon &lt; j_{\text{lim,Sn}} + j_{\text{lim,Co}}$</td>
<td>$X_{Co} = 1 - \frac{j_{\text{lim,Sn}}}{j \varepsilon}$</td>
<td>7.38 (a)</td>
</tr>
<tr>
<td>$j_{\text{lim,Sn}} + j_{\text{lim,Co}} = j \varepsilon$</td>
<td>$X_{Co} = \frac{j_{\text{lim,Co}}}{j_{\text{lim,Sn}} + j_{\text{lim,Co}}} = \frac{D_{Co} C_{Co}}{D_{Co} C_{Co} + D_{Sn} C_{Sn}}$</td>
<td>7.39 (a)</td>
</tr>
<tr>
<td>$j_{p} &lt; j_{\text{P,L,Sn}}$</td>
<td>$X_{Co} = 0$</td>
<td>7.37 (b)</td>
</tr>
<tr>
<td>$j_{\text{lim,Sn}} &lt; j_{p} \varepsilon &lt; \frac{j_{\text{lim,Sn}} + j_{\text{lim,Co}}}{\theta}$</td>
<td>$X_{Co} = 1 - \frac{j_{p,Sn}}{j_{p} \varepsilon}$</td>
<td>7.38 (b)</td>
</tr>
<tr>
<td>$\frac{j_{\text{lim,Sn}} + j_{\text{lim,Co}}}{\theta} = j_{p} \varepsilon$</td>
<td>$X_{Co} = \frac{D_{Co} C_{Co}}{D_{Co} C_{Co} + D_{Sn} C_{Sn}}$</td>
<td>7.39 (b)</td>
</tr>
</tbody>
</table>

From Equation 7.40 we can also obtain that the average current density corresponding to the pulse limiting current density will never be higher than the limiting current density under direct current conditions. This implies that the curves of the cobalt content in the deposits plotted against the average current density for pulse electroplating should always stand at the left hand side of the curve for direct current electroplating and the operation window for pure tin layers should become narrower under pulsed current conditions. This
trend was confirmed in Figures 7.27 and 7.29. It is also in good agreement with the results of the Hull cell tests (Figure 7.20). Therefore, in terms of the operating window for pure tin layers there are not any advantages in using pulsed current. That is the reason why we used direct current for pure tin layers during the electrodeposition of tin-cobalt alloy multilayer coatings.

To further explain the relative position of the composition curves, e.g. Figures 7.28 and 7.29, the relationship between the pulse limiting current density and the pulse parameters is examined. Combining Equations 7.19 and 7.26 and after rearranging, one obtains

$$\frac{J_{pl}}{J_{lim}} = \frac{1}{\theta + \sqrt{2Dt_{on}}(1-\theta)^{\frac{3}{2}}}$$  (7.41)

In Equation 7.41, the term $\sqrt{2Dt_{on}}$ is the diffusion layer thickness after the first pulse and note $\delta_p = \sqrt{2Dt_{on}}(1-\theta) < \sqrt{2Dt_{on}} < \delta_N$. For current waveforms with a fixed on-time, $\frac{\sqrt{2Dt_{on}}}{\delta_N}$ is a constant smaller than 1. Values of $\frac{J_{pl}}{J_{lim}}$ calculated from Equation 7.41 are shown in Figure 7.101. Consider the current waveforms of a constant on-time but varied off-time. Since the duty cycle decreases with increase in the off-time, the corresponding pulse limiting current density increases according to Figure 7.101. This explains the shift of the curves with variation of off-time in Figure 7.28. Note that Equation 7.41 only gives an approximated description of the relationship between the pulse limiting current density and the pulse parameters. For more accurate calculation the analytical solution in Equation 4.20 has to be used.

7.6.2.3.4 Effect of frequency

The effect of frequency on the cobalt content in the deposits shows a strong dependence on the duty cycle and the average/peak current density as shown in Figure 7.25. Such dependence can be predicted according to Figure 7.100. On the basis of Figure 7.100, for a current waveform with a fixed duty cycle, with increase in the frequency from very low to very high values, the average peak current density for the deposition of tin, $J_{p,Sn}$, at a given applied peak current density, $j_p$, (or a given average current density for a fixed duty
cycle), increases from $j_{\text{lim,Sn}}$ to $\frac{j_{\text{lim,Sn}}}{\theta}$. Since the current efficiency, $\varepsilon$, was found not to vary appreciably within the frequency range investigated (Figure 7.30), the increase in $j_{p,Sn}$ leads to a decrease in the cobalt content in the deposit with increasing the frequency according to Equation 7.38(b). At the same time, the cobalt content of the deposits under two extreme situations can be expressed as:

$$X_{Co} = 1 - \frac{j_{p,Sn}}{j_p \varepsilon} = 1 - \frac{j_{\text{lim,Sn}}}{j_p \varepsilon} \quad \text{at very low frequency} \quad (7.42)$$

$$X_{Co} = 1 - \frac{j_{p,Sn}}{j_p \varepsilon} = 1 - \frac{j_{\text{lim,Sn}}}{\theta j_p \varepsilon} \quad \text{at very high frequency} \quad (7.43)$$

Comparing Equations 7.42 and 7.43 with Equation 7.38(a), it can be found that the deposit composition at very low frequencies corresponds to that of direct current electroplating with a current density $j = j_p$, whilst the deposit composition at very high frequencies corresponds to that of a direct current electroplating with a current density $j = j_m$. Taking the current waveform with a duty cycle of 50% as an example, we can thus predict that at the same average current density of 1 A/dm$^2$, the cobalt content in the deposits obtained at very low frequencies will tend to be equal to that of the deposit plated at the corresponding peak current density of 2 A/dm$^2$ under direct current conditions, which is approximately 14 wt.%. At very high frequencies, the deposition composition will tend to be equal to that of the deposit plated at the average current density of 1 A/dm$^2$, which is approximately 6 wt.%. The predicted trend of the variation of the deposition composition with the frequency at a fixed average/peak current density and the corresponding experimental data are schematically illustrated in Figure 7.102. These experimental data points prove that the prediction is reasonable. It must also be pointed out that at very high frequencies the capacitance effect may occur and dominate the deposition process. Therefore, the mass transport theory is only valid up to a certain frequency. Fortunately the damping of the faradaic current due to the capacitance effect leads to the same consequence as predicted by mass transport theory, namely, pulse electroplating at very high frequencies is virtually a direct current one carried out at the corresponding average current density.
Similar trends also hold for other average current densities, e.g. 2 A/dm$^2$ (Figure 7.102). At even higher average current density, both the deposition of tin and the deposition of cobalt at all frequencies are under mass transport control and therefore the composition of the deposits is decided by the composition of the electrolyte according to Equation 7.39. No dependence on the frequency can be observed anymore. For a duty cycle of 20% (Figure 7.25(c)), no effect of frequency was observed within the frequency range from 5 to 200 Hz. This was due to the fact that the investigated frequency was not sufficiently high, due to the limitation from the pulse generator.

7.6.3 Mechanism of the effect of Tween 20

It has been established in Section 7.2 that the non-ionic surfactant, Tween 20, played an important role in the electrodeposition of acceptable tin-cobalt alloy deposits. Without addition of Tween 20, the deposits were black, non-adherent, and dendritic within the whole current density range studied (Figure 7.23). This phenomenon can be attributed to the fact that tin, which is the main component (more than 80 wt.% in the tin-cobalt alloys obtained in this research, is prone to the formation of dendrites from acid stannous solution in the absence of any addition agents [50, 194-195]. This characteristic of tin (or tin in tin-cobalt alloys) was due to the very low activation polarisation associated with the deposition process, as revealed by the result of the potentiodynamic polarisation study in the acid sulfate/gluconate solution in the absence of Tween 20 (Figure 7.62). On the other hand, with addition of Tween 20, a considerable improvement was observed on tin-cobalt alloy deposits in terms of adherence and freedom from dendrites (Figure 7.23). For the same reason as that in the absence of Tween 20, the substantial increase in the cathode polarisation for the deposition of tin in the presence of Tween 20 in the electrolyte (Figures 7.62 an 7.65) is responsible for this improvement.

Although the modification of the morphology of tin-cobalt alloy deposits by Tween 20 could be interpreted in the context of increased cathode polarisation, it is difficult to propose a consistent and detailed explanation on why addition of Tween 20 could change the shape of the polarisation curves and increase the cathode polarisation for the deposition of tin-cobalt alloys, due to the limited experimental data available. However, the following features of the behaviour of Tween 20 can be cited:
CHAPTER 7 RESULTS AND DISCUSSION

- Tween 20 is effective at very small concentrations, e.g. 0.1 ml/l (Figure 7.65). The inhibition of the cathodic process by Tween 20 then quickly levels off with increase in concentration in the solution.

- The effect of Tween 20 is selective and specific. Tween 20 was found to be effective for the deposition of tin, but had no effect on the deposition of cobalt. (See Figures 7.62 and 7.63)

- The effect of Tween 20 is potential dependent. Tween 20 does not affect the onset of the deposition of tin and the deposition rate of tin at a given potential was slowed down only after the cathode potential was more negative than a certain critical potential. This critical potential is a function of pH (Figure 7.78), the concentration of Tween 20 (Figure 7.65) and tin(II) ions (Figure 7.77), and it is also affected by the addition of boric acid (Figure 7.86)

- In the presence of Tween 20 agitation exhibited much less depolarising effect on the deposition of tin-cobalt alloys than in the absence of Tween 20 (Figures 7.65 and 7.66).

- The main peculiarity of the action of Tween 20 on the polarisation behaviour during the deposition of pure tin or tin-cobalt alloys is that with addition of Tween 20, the deposition rate of tin decreases sharply to a minimum and then increases slowly with increase in the cathodic overpotential.

Considering that Tween 20 is a non-ionic surfactant and non-ionic surfactants have high affinity for interfaces due to their hydrophobic groups, it is not difficult to propose that Tween 20 functions by being adsorbed or accumulating in some way at the cathode/electrolyte interface during the electrodeposition of tin-cobalt alloys. In fact, an adsorption mechanism [196-200] is a commonly accepted explanation of the influence of organic compounds on the deposition kinetics and deposit properties, e.g. Tritons in the electrodeposition of tin from acid electrolyte [194-195], polyethylene glycol (PEG) in the deposition of copper [201-204], and saccharin and thiourea [205] in the electrochemical preparation of soft magnetic CoNiFe films. The adsorption of organic additives has been confirmed in situ by means of some non-electrochemical techniques such as Raman spectroscopy [206].

With regard to the adsorption of Tween 20 on the cathode, one of the important parameters of concern is its critical micelle concentration (CMC) in the electrolyte, as the formation of
micelles may strongly influence its adsorption isotherms [194]. According to reference
[207], the CMC of Tween 20 in aqueous solution at 25°C is 0.006 g/l (approximately
0.0054 ml/l) and this value might be expected to shift to even lower values with the
increase of electrolyte temperature. The extremely low CMC of Tween 20 is probably the
reason why it is effective even at the concentration of 0.1 ml/l at the working temperature
of 45-50°C. Following the same reasoning the saturation of the cathode surface with
adsorbed Tween 20 molecules and the formation of micelles in the bulk solution with
further increase in its concentration above the CMC, explains the phenomenon that the
effect of Tween 20 quickly levels off at higher concentrations.

On the other hand, neutral organic molecules generally tend to adsorb to the greatest extent
on an uncharged electrode [208]. As the electrode becomes charged (positively or
negatively ) the neutral molecules are displaced by oriented water molecules whose dipole
charges become attracted to the electrode or by specifically adsorbed anions (for a
positively charged electrode). If the adsorption of Tween 20 on the cathode also follows
the tendency for neutral organic molecules, then the sharp decrease in the current density
due to the addition of Tween 20 at a certain potential is understandable. Also, it might be
expected that the potential of zero charge ( PZC ) of the cathode is more negative than the
onset potential for the deposition of tin, and addition of boric acid shifts the PZC markedly
to a less negative potential (Figure 7.85). The effect of boric acid on the PZC may be
reasonable as both Horkans [209] and Yin [210] have reported that boric acid could adsorb
on the cathode during the electrodeposition of nickel and nickel-iron alloys. However,
additional experiments are needed to confirm this explanation.

It is also possible that the sharp decrease in the cathodic current density beyond a critical
potential has nothing to do with the PZC at all, because Tween 20 inhibits effectively the
deposition of tin within a very wide potential range, which is revealed in the investigation
of the effect of agitation (Figures 7.72 and 7.73). There is no indication that Tween 20
desorbed from the cathode even at very negative potentials. Therefore, it is probable that
the adsorption of Tween 20 on the electrode becomes significant only beyond the critical
potential observed. In the literature it has been established that polyethylene glycol (PEG)
is adsorbed on the surface of copper in the potential range for copper deposition, but not at
the open circuit potential [206]. In Galdikiene and Mockus’ study [211] on the cathodic
process in copper-tin deposition from sulfate solutions, they also observed that in the
presence of polyether Laprol 2402C, after the deposition rate of copper-tin alloys reaches a maximum there is a sharp decrease in the cathodic current, which is then followed by a sharp increase. However, no explanation was made on this phenomenon except a suggestion of complex interactions between the electrode surface and the solution components.

The adsorbed Tween 20 may change the reduction kinetics and the electrocrystallisation processes of tin/tin-cobalt alloys in several ways, producing a large incremental increase in the cathodic polarisation. First, Tween 20 may adsorb on the active sites of the crystal planes of the substrates and on the emerging surfaces of the crystallizing phases themselves, thus leading to physical blocking of these preferential growth sites and diverting the current flow to less preferential ones, where more energy is essential for the nucleation and growth of metals \[194, 211-213\]. A blocking mechanism implies a partial coverage of the surface by the adsorbates. Secondly, Tween 20 may adsorb over the entire cathode surface and form a relatively thin, complete layer of Tween 20 molecules. This "semi-insulating" layer creates an added energy barrier for the charge transfer process \[194, 199\] and consequently make the charge transfer process the rate-determining step. Finally, with thickening of the adsorbed layer of Tween 20, it is also probable that the reduction rate of tin ions is predominated by the diffusion of tin ions through the layer prior to their reduction \[214\]. The formation of this thick barrier is kinetically limited rather than diffusion controlled. Therefore, agitation only has limited influence and Tafel linearity is not expected with this mechanism.

The first suggested mechanism seems unlikely as the concentration of Tween 20 in the solution is much higher than the CMC. The coverage of Tween 20 on the cathode is expected to be high. If the second mechanism is applicable, then according to Meibuhr \[194\] there should exist a potential range within which the polarisation would be expected to depend logarithmically on the current density. However, in our experiments no such Tafel linearity was observed. This might indicate that the third mechanism, i.e. the thick adsorption layer of Tween 20, is more likely. Aragon and co-authors \[212\] have proposed that when additive concentrations are equal to or higher than the CMC, high molecular weight micelles are formed. These micelles form a thick layer constituting a membrane, anchored in the sites of highest energy on the electrode. This proposal seems also applicable to the adsorption of Tween 20 on the deposition of tin electrode.
CHAPTER 7 RESULTS AND DISCUSSION

The selective or specific suppression of the electrodeposition of tin by Tween 20 (no effect on cobalt) makes the mechanism of action more complicated. However, the selective influence of adsorbed cathode layers on the deposition of one component is a phenomenon frequently observed during the electrodeposition of alloys [211, 214-219]. A typical example is the anomalous codeposition of alloys, such as Ni-Fe[184] and Zn-Fe/Co/Ni [215]. It has been postulated that the anomalous codeposition is related to the formation of and reduction of insoluble films of the less noble metal, which at the same time inhibits the deposition of the other metal. It should be noted that this is only one of several proposed mechanisms [220, 221]. The difference in the suppression effect found for tin and cobalt deposition with addition of Tween 20 could be explained by (a) the adsorbed Tween 20 layer acting as a molecule sieve and due to the difference in the ionic radii of tin and cobalt ions, Tween 20 may only slow down the mass transport of tin ions but allow free transport of cobalt ions to the cathode. This mechanism has been proposed by Goodenough and Whitlaw [217] for the different suppression effect on the deposition of tin and lead by a non-ionic ethoxylated surfactant. (b) Tween 20 may form a complex selectively with the intermediate products of Sn(II) reduction (Sn(I) adions or Sn adatoms ) adsorbing on the cathode [219]. Cyclic voltammetry studies by Vasantha et al. [218] have indicated that the weak adsorption of peptones hindered the reduction of the intermediate Sn(I) to Sn. On the deposition of bright copper coatings from acid solutions it was suggested that the formation of complexes of Cu⁺ and Cu²⁺ with polyethylene glycol and Cl⁻ and their possible adsorption on the cathode surface may be responsible for the increased polarisation and the brightening effect [203-204]. Therefore, the above-mentioned two mechanisms are both reasonable for the selective effect of Tween and it is difficult to preclude either of them without additional experiments.

7.6.4 Fatigue strength of multilayer overlays

Although there has been no generalised conclusions regarding the factors contributing to the property enhancement of CMM coatings, experimental evidence reported in the literature suggests that the properties of CMM coatings are a function of

- the thickness of individual layers [147],
- the ratio of the individual layer thickness,
• the identity of individual layers, including the composition, microstructure and the sharpness of the interfaces [118, 147, ]
• the stacking sequence of layers [122, 167]
• the overall thickness of the CMM coatings.

However, as shown in Tables 7.17 and 7.18, the fatigue strength of the Sn-Co alloy multilayer overlays did not show any significant dependence on the thickness configuration of individual layers. This independence of the fatigue strength on the thickness configuration may be due to the fact that the individual layers were not thin enough. In the literature, the tensile strength results by Menezes et al. [147] show that the strength increases rapidly only after the layer spacing is smaller than 40nm, although Tench and White [144] has also reported that the tensile strength of Cu/Ni CMM coatings is a weak function of the layer spacing. In addition, as revealed by the cross-section of plain bearings, the control of the individual layer thickness or the quality of the multilayered structure of the overlays, was also problematic. In particular, the actual thickness of the pure tin layers were only deposited to the designed value for the first layer (Figure 7.45). Since the reduced thickness of pure tin layers during the subsequent deposition was only observed in samples plated using the slotted electroplating jig (Figure 6.3), this phenomenon was thought to be a consequence of either the depletion of tin ions in the electroplating jig, or an increase in the pH value of the solution confined in the electroplating jig. Therefore, the application of appropriate agitation for the present electroplating process seems necessary to circulate and replenish fresh solution into the jig.

On the other hand, it seems that the fatigue strength of the multilayer overlays from an electrolyte with 20% cobalt is on average higher than that from an electrolyte with a cobalt content of 15%. This enhancement may be due to the increased magnitude of the composition modulation between the Sn-Co alloy layers and the pure tin layers. Under the given electroplating the nominal composition of alloy layers in the multilayer overlays were approximately 18 wt.% from the solution containing 20% cobalt (Figure 7.28 (a)), and approximately 10 wt.% from the solution containing 15% cobalt (Refer to Tables 7.15 and 7.16). The Sn-Co alloy layers with higher cobalt content have higher microhardness (Tables 7.15 and 7.16) and therefore have higher resistance to the formation of persistent slip bands (PSBS), which leads to the nucleation of fatigue cracks [161] on the surface. However, as also pointed out by Stoudt et al. [161], for the optimum resistance to fatigue
crack nucleation a surface coating needs a combination of properties including hardness, toughness, cyclic working hardenability, residual compressive stresses, and adherence. Although the multilayer overlays deposited from the solution containing 15% cobalt have a compressive residual stress which may help to reduce the magnitude of the tensile stresses in the coating (Figure 7.54), the fatigue strength of the corresponding multilayer overlays is lower than that of the overlays from the solution containing 20% cobalt, which have a tensile residual stresses (Figure 7.55). Therefore, the effect of residual stress in the coating is not significant for these Sn-Co alloy multilayer coatings. The possible explanation for this is that the magnitude of the residual stresses are not sufficient to be detrimental (i.e. < 60 MPa as shown in Figures 7.54 and 7.55).

Although the deflection of fatigue cracks was observed over the cross-section of plain bearings deposited with Sn-Co alloy multilayer overlays, this phenomenon should not be regarded as a strengthening mechanism, as the fatigue strength measured is the resistance of the coating to the fatigue crack initiation, whereas the deflection represents how the fatigue crack propagates in the coating. This explains why the deflection of fatigue cracks could be observed in all samples with high or low fatigue ratings.
8 Conclusions and Further Work

8.1 Conclusions

Experimental investigations carried out in this thesis have led to the successful electrodeposition of compositionally modulated tin-cobalt alloy multilayer coatings as overlays on the surface of plain bearings. In addition, some efforts have also been made to understand the codeposition mechanism of tin-cobalt alloys from a new sulfate/gluconate bath. From these investigations, the following conclusions may be drawn:

8.1.1 Electrodeposition of Sn-Co alloys

- The standard commercial ACHROLYTE process is not suitable for the electrodeposition of compositionally modulated Sn-Co alloy multilayer coatings. A rapid decrease in the cobalt content of deposits obtained was found with a small increase in the current density and no pure tin could be deposited from this bath. The lowest cobalt content of deposits from this bath is approximately 10 wt.%. In addition, the very low current efficiency for prolonged electroplating durations was also a disadvantage.

- A new sulfate/gluconate electrolyte was established. The codeposition of tin and cobalt from this electrolyte was confirmed to form a regular alloy codeposition system. At low current densities pure tin was deposited, whereas the cobalt was codeposited with tin only after the applied current density exceeded the corresponding limiting current density for the deposition of tin. With increase in current density, the cobalt content in the deposits increases until reaching the percentage cobalt content in the solution. This deposit composition-current density relationship makes possible the deposition of the desired compositionally modulated Sn-Co alloy multilayer coatings using the single bath technique.
• The pH value of the electrolyte is critical for the deposition of acceptable Sn-Co alloys. The optimum pH value is 3.5-4. At a pH value of 1-2, the deposition of tin and the evolution of hydrogen are the main electrode reactions, and no or little cobalt was detected in the deposits obtained. At a pH value 5-6, the desired deposit composition-current density relationship was not possible. Even higher pH values lead to the hydrolysis of tin(II) and instability of the solution.

• The total metal concentration and the agitation strength of the electrolyte were found to have the most significant effect on the current density ranges for the codeposition of cobalt with tin. These factors which increases the limiting current density for the deposition of tin, shifts the current density range for the codeposition to higher current densities.

• Although the concentration ratio of Sn(II) to Co(II) ions, the concentration of sodium gluconate, the supporting electrolyte (sodium sulfate), and the operating temperature did not exhibit significant influence on the current density range for the alloy codeposition, they had noteworthy effects on the cobalt content in the deposits.

• The main function of sodium gluconate in the electrolyte is to stop the divalent tin(II) ions from hydrolysis. To be effective, the molar ratio of sodium gluconate to tin(II) ions must be at least 1.5. However, with increase in the concentration of sodium gluconate, the alloy deposits tend to become dark and dendritic, which was accompanied by a decreased cobalt content in the deposits. Sodium gluconate has negligible effect on the cathodic current efficiency.

• Both Tween 20 and boric acid were essential for the deposition of acceptable Sn-Co alloy deposits. The cobalt content in the deposit increases with the addition of Tween 20 and levels off at concentrations higher than 4 ml/l. Addition of Tween 20 only slightly decreases the deposition efficiency. It was found, by titration, that the addition of boric acid actually enable the hydrolysis reaction of tin(II) ions to occur at lower pH values, in spite of its improved electrocrystallisation effect.
CHAPTER 8 CONCLUSIONS AND FURTHER WORK

8.1.2 Pulse electroplating

- From the result of Hull cell tests, pulse electroplating was found to be effective in preventing the formation of dendrites during prolonged deposition of tin-cobalt alloys. With appropriate pulsed current parameters, the workable current density range for Sn-Co alloys may be widened.

- For pulsed current waveforms with lower duty cycles (e.g. < 20%), the composition of Sn-Co alloy deposits obtained within the current density range from 1 to 4 A/dm$^2$ is nearly a constant, suggesting a remarkably improved uniformity of the alloy composition distribution in the coating. This phenomenon is caused by the very high instantaneous peak current density at low duty cycles. Under such conditions, the actual deposition process is under mass transport control.

- For a current waveform of a given duty cycle, the cobalt content in the deposits decreases as the frequency increases. At low frequencies, the mass transfer through the pulsating diffusion layer is the rate-limiting step and thus the deposits obtained have a composition equivalent to that of a coating deposited at the corresponding peak current density using the direct current. On the contrary, at higher frequencies, the mass transfer through the stationary diffusion layer is the rate-limiting step and consequently, the deposits have a composition equivalent to that of a deposit plated at the corresponding average current density using direct current. In addition, the capacitance effect may be relevant at very high frequencies, which also leads the deposition to become a direct current one.

- The frequency of the pulsed current did not show a considerable effect on the deposition efficiency of Sn-Co alloys. The measured cathodic current efficiency was mainly a function of the duty cycle and the average current density and it may be slightly higher than that under direct current conditions.

- The selective dissolution of the less noble component, cobalt, during the off-time was ruled out with AES depth profiling. This was further confirmed by the fact that the electrode potential difference between tin an cobalt in the solution is too small.
Meanwhile, the microstructure and the composition of the Sn-Co alloys studied do not satisfy the requirements for the selective dissolution of cobalt.

- Following a detailed analysis of Ibl’s duplex diffusion layer mathematical model for pulse electroplating, the effect of pulse parameters on the deposition behaviour of a regular codeposition system was explained on the basis of the mass transport control. The main finding is that the actual deposition rate of the more noble metal, i.e. tin, may be slowed down by using pulsed current and thus enhancing the deposition of the less noble metal, which is either under kinetic control or under mass transport control depending on the pulse parameters.

8.1.3 Sn-Co alloy multilayer coatings

- Tin-cobalt alloy multilayer coatings were deposited from a single electrolyte onto both copper substrate and the surface of plain bearings as overlays. The cross-sectional examination showed well-defined interfaces between different layers. The composition modulation was further confirmed by X-ray elemental mapping.

- The grain size of a single layer deposit of pure tin is a function of the deposit thickness. Coarse pyramidal grains were obtained with thick deposits. In multilayer coatings, grain refinement was observed as the deposit thickness of individual layers of pure tin was decreased. Conversely, the grain size of a single layer deposit of Sn-Co alloys is independent of the deposit thickness. The variation of the thickness of individual layers of Sn-Co alloys in multilayer coatings exhibited negligible effect on the grain size of the outmost layer of pure tin.

- The microhardness of single layer coatings of pure tin was found to be approximately 13 HV. Sn-Co alloy deposits are much harder (91-653 HV), and their microhardness increases with increasing cobalt content.

- The internal stress in single layer coatings of pure tin is compressive. Depending on the solution formulation, the internal stress in single layer coatings of Sn-Co alloys may be compressive or tensile. The average internal stress of a multilayer coating has an
intermediate value situated between the two stresses for the equivalent single layer coatings of both sublayer compositions respectively. With variation of the thickness configuration, the average internal stress in multilayer coatings may be further modified. Since the absolute values of the average internal stress in multilayer coatings are small (< 60 MPa), it was later found that the effect of internal stress on fatigue strength is not significant.

- The fatigue strength of multilayered overlays on plain bearings was more dependent on the electrolyte formulation (or in fact the magnitude of the composition modulation) rather than the thickness configuration of individual layers. The average fatigue strength of multilayered overlays was within the range of 69-83 MPa, with the highest value being 90 MPa.

- The SEM observation of the cross-sections of plain bearings after fatigue tests shows that during the propagation in the multilayered overlay, the fatigue cracks may change their directions at the interfaces on reaching the hard Sn-Co alloy sublayers.

8.1.4 Potentiodynamic polarisation studies

- For the deposition of pure metals, Tween 20 suppresses the deposition of tin within a wide electrode potential range, but has no significant effect on the deposition of cobalt. Similar suppression of the tin deposition reaction was also observed during the potentiodynamic polarisation study on the electrodeposition of Sn-Co alloys.

- Only 0.1ml/l Tween 20 was needed for it to be effective and the suppression effect quickly became saturated with increasing concentrations of Tween 20 having little more effect.

- The first peak on the cathodic polarisation curves for the deposition of tin and tin-cobalt alloys with addition of Tween 20 were not dependent on the substrate materials, the potential sweep rate or mode (potentiodynamic or potentiostatic) or direction. Therefore, its occurrence must be due to the unique interaction between Tween 20 and the deposition process of tin rather than the experimental methods.
As a non-ionic surfactant, Tween 20 was thought to adsorb on the cathode surface and form a film. The extent of this film formation is governed by the rate of adsorption and the adsorption equilibrium, both of which depend on the electrode potential.

The selective effect of Tween 20 on the deposition process of tin rather than cobalt was attributed to either the slow penetration of tin ion species through the adsorbed film and the selective movement of cobalt ion species through the layer. A further possibility could be the selective formation of complexes of Tween 20 with ionic tin species.

The pH value of the solution has a marked effect on the deposition reaction of tin and cobalt. With increasing pH value, the polarisation resistances for the deposition of tin, cobalt or tin-cobalt alloys were all increased, with the polarisation curves shifting towards more negative potential values and the limiting current density being decreased.

Addition of boric acid was found to intensify the suppression effect of Tween 20 on the deposition process of tin and shift the critical potential for Tween 20 to be effective to more positive electrode potentials.

8.2 Suggestions for further work

The results of preliminary fatigue tests indicate that Sn-Co alloy multilayer coatings are a promising substitute for the traditional lead-based alloy overlays for plain bearings. However, a fatigue strength higher than 100 MPa has recently been proposed as the minimum requirement for the potential application by the automotive industry, which has not been achieved so far with the multilayered overlays. Therefore, any further work should centre around the attempts to increase the fatigue strength of any lead-free overlays. The suggestions for further work are:

Introduction of appropriate agitation into the electroplating jig to stop the solution trapped in it from becoming depleted in reducible ions and also to prevent the pH value
of the solution from increasing to a detrimental level. This should allow the thickness configuration of multilayer coatings to be controlled to the designed values. Mechanical movements of the cathode or pumping the fresh solution into the slotted jig may be the practical options.

- An investigation into the fatigue strength of Sn-Co alloy multilayer overlays with thinner thickness of individual layers, e.g. < 0.5 μm. It is expected that with decreasing layer spacings, the hardness of the multilayer overlays and consequently their resistance to the nucleation of fatigue cracks may be increased. However, there is a limitation over the minimum thickness obtainable for each layer to form a continuous phase rather than isolated crystals.

- Maintaining the cobalt content in the solution as about 20%. Too low a cobalt content in the solution decreases the composition modulation in the deposits. Too high a cobalt content in the solution makes the deposition of pure tin sublayers difficult and at the same time increase the brittleness of the alloy sublayers as a result of increased cobalt content in the deposits.

- Adoption of three-point bending fatigue tests [222] in the laboratory to assess the fatigue properties of multilayer overlays to speed up the optimisation process for the optimum parameters of thickness and composition configuration of multilayer coatings. Samples under optimised conditions will then be subjected to the standard fatigue test using the Sapphire fatigue testing machine which replicates the in-service loading and takes about one week or more for one sample.

- Electrodeposition of bimetal multilayer overlays, such as Sn/Ni, Sn/Cu, Sn/Zn, or less likely Sn/Co, using dual bath techniques for fatigue assessments. The reason for adopting these new systems is to increase the ductility of the coating and the sharpness of the interfaces between individual layers. The potential bath contamination associated with the dual bath technique should not be problematic as the purity of individual layers is not crucial for the tribological application. The main problems of concern are probably the oxidation of the deposited layers and the displacement reaction on
depositing the more noble layers, which are detrimental to the adherence between individual layers.
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Figure 1.1 Schematic illustration of the desired structure of compositionally modulated Sn-Co alloy multilayer coatings as overlays for plain bearings. The application of a nickel barrier depends on the material of the bearing substrates. It was only deposited on the surface of aluminium alloy bearings, but not on lead-bronze bearings in the present research.
**Figure 2.1** Examples of plain bearings

**Figure 2.2** Schematic illustration of the structure of a typical plain bearing
Figure 2.3 Cross-section of a plain bearing, showing the fatigue failure of a lead-tin overlay (after Forrester [21]).

Figure 2.4 Effect of coating thickness on fatigue strength of electrodeposited lead-based overlays (after Bhushan [5]).
Figure 3.1 Thermal equilibrium phase diagram of tin-cobalt alloys [54]
Figure 4.1 Examples of sinusoidal waveforms (after Oscro [69])
Figure 4.2 Examples of square waveforms (after Puippe [68])
Figure 4.3 Parameters of a square waveform

Figure 4.4 Nernst diffusion layer model under direct current conditions
Figure 4.5 Schematic concentration profile at the cathode for pulsed current plating

Figure 5.1 Schematic illustration of an electrodeposited CMM coating

A/B combinations
- Metal/Metal
- Metal/Alloy
- Alloy/Alloy
Figure 5.2 An automated dual bath electrodeposition system eliminating the interbath transfer of the substrate. (After Ross et al. [127])

Figure 5.3 Schematic illustration of the typical cathodic polarisation curve suitable for the deposition of CMM coatings from a single electrolyte. $E_A^0$, and $E_B^0$ are the equilibrium potentials for metal A and B, respectively. (After Gamburg [120])
Figure 5.4 Schematic representation of the potential response and corresponding partial current changes with time during the deposition of CMM coatings under the single current pulse regime. (a) displacement reaction occurs during the off-time (After Despić and Jović [142]), (b) no displacement reaction occurs during the off-time (after Gamburg [120])
Figure 6.1 Schematic illustration of desired relationship between the deposit composition and the applied current density.

Figure 6.2 Plating sequence for the electrodeposition of compositionally modulated Sn-Co alloy multilayer coatings.
Figure 6.3 Jig assembly for electroplating bearings
Figure 6.4

Experimental set-up for internal stress measurement (Bending strip method)
Figure 7.1 Effect of current density on the composition of deposits obtained from Achrolyte solution.
Figure 7.2 Effect of current density on the surface morphology of deposits from the Achrolyte solution
Figure 7.3 Variation of deposit composition and current efficiency of Sn-Co alloy with the tin sulphate concentration at two different current densities (after Rehim et al [44]). (a) 3A/dm$^2$, (b) 10A/dm$^2$. The broken line AB indicates the composition reference line which represents the metal percentage of cobalt in the bath.

Figure 7.4 Deposit composition-current density relationship obtained from the new sulphate/gluconate bath for the deposition of Sn-Co alloys
Figure 7.5 Surface morphology of coatings deposited from the new sulphate/gluconate bath
Figure 7.6 Effect of cobalt content in the solution on the composition of deposits from the new sulphate/gluconate bath

Figure 7.7 Effect of solution pH on the composition of deposits from the new sulphate/gluconate bath
Figure 7.8 Effect of diluting/concentrating the standard sulphate/gluconate bath (Table 6.2) on cobalt content in deposits.

Figure 7.9 Effect of sodium gluconate concentration on the cobalt content in deposits from the new sulphate/gluconate bath.
Figure 7.10 Effect of sodium sulphate concentration on the cobalt content in deposits from the new sulphate/gluconate bath

Figure 7.11 Effect of agitation level on the cobalt content in deposits from the new sulphate/gluconate bath
Figure 7.12 Effect of agitation level on the cobalt content in deposits from a 3-fold concentrated sulphate/gluconate bath.

Figure 7.13 Effect of solution temperature on the cobalt content in deposits from the new sulphate/gluconate bath.
Figure 7.14 Results of Hull cell tests on the new sulphate/gluconate solution in Table 6.2 with the addition of different concentrations of gelatine
Figure 7.15 Results of Hull cell tests on the new sulphate/gluconate solution in Table 6.2 with the addition of different concentration of Tween 20.
Figure 7.16 Results of Hull cell tests on the new sulphate/gluconate solution (Table 6.2) containing 2g/l gelatine and various concentrations of Tween 20
Figure 7.17 Effect of off-time on the appearance of deposits obtained from the solution given in Table 6.3. The on-time remained a constant of 1 ms.
Figure 7.18 Effect of off-time on the composition of tin-cobalt alloy deposits from the solution given in Table 6.3. (a) plotted against peak current density, (b) plotted against average current density
Figure 7.19 Effect of off-time on the cathodic current efficiency for the deposition of tin-cobalt alloys from the solution given in Table 6.3. (a) plotted against peak current density; (b) plotted against average current density
Figure 7.20  Effect of duty cycle on the Hull cell current density ranges for the deposition of tin-cobalt alloys from the solution given in Table 6.4
Figure 7.21  Micrographs showing the morphologies of deposits from different zones on a Hull cell panel. (See Table 6.4 for the electrolyte)
Figure 7.22 (continued)
Figure 7.22 (continued)
Figure 7.22 (continued)
Figure 7.22 Effect of frequency at different duty cycles on Hull cell patterns from the solution given in Table 6.4
Figure 7.23 Hull cell patterns with the addition of different concentrations of Tween 20 to the solution given in Table 6.4
Figure 7.24 Hull cell patterns from solutions with different cobalt contents. The concentration of tin sulphate and cobalt sulphate in the solution are given in Table 7.5. These solutions also contained 120g/l sodium gluconate, 30g/l boric acid, 20g/l sodium sulphate and 4ml/l Tween 20. The pH value was 4 and the temperature was 45-50°C.
Figure 7.25 (continued)
Figure 7.25  Effect of frequency of pulsed current on the deposit composition at different duty cycles and average current densities (1-4 A/dm²). The solution used is given in Table 6.4.
Figure 7.26 Effect of on-time on the deposit composition under the condition of constant off-times, plotted against the peak current density. The solution used is given in Table 6.4.
Figure 7.27 Effect of on-time on the deposit composition under the condition of constant off-times, plotted against the average current density. The solution used is given in Table 6.4.
Figure 7.28 Effect of off-time on the deposit composition under the condition of constant on-times, plotted against peak current density. The solution used is given in Table 6.4.
Figure 7.29 Effect of off-time on the deposit composition under the condition of constant on-times, plotted against the average current density. The solution used is given in Table 6.4.
Figure 7.30 (continued)
Figure 7.30 (continued)
Figure 7.30 (continued)

(e) duty cycle = 33%

(f) duty cycle = 20%

Figure 7.30 (continued)
Figure 7.30 Effect of frequency on current efficiency for pulsed current waveforms with different duty cycles. The solution used is given in Table 6.4.

Figure 7.31 Effect of duty cycle on the cathodic current efficiency at the same average current densities. The solution used is given in Table 6.4.
Figure 7.32 Effect of Tween 20 on cobalt content in deposits under different conditions. (a) 20% cobalt in solution, PC1-1ms, \( i_a = 3 \) A/dm\(^2\) (b) 15% cobalt in solution, PC1-1ms, \( i_a = 3 \) A/dm\(^2\) (c) 20% cobalt in solution, DC, \( i = 0.5 \) A/dm\(^2\) (d) 15% cobalt in solution, DC, \( i = 0.5 \) A/dm\(^2\)

Figure 7.33 Effect of Tween 20 on current efficiency in the solution containing 20% cobalt in metal percentage
Figure 7.34 Effect of sodium gluconate on the deposit composition

Figure 7.35 Effect of sodium gluconate on cathodic current efficiency.

(a) DC $i = 0.5 \text{ A/dm}^2$
(b) DC $i = 3 \text{ A/dm}^2$
(c) PC1-2ms, $i_a = 3 \text{ A/dm}^2$
Figure 7.36 Surface morphology of single layer/multilayer coatings.

The total thickness of all these coatings is approximately 12 μm.
Figure 7.37 Surface morphology of tin-cobalt alloy multilayer coatings with varying thickness of pure tin sublayers. These sublayers were deposited using direct current at 0.5 A/dm² and tin-cobalt alloy sublayers were deposited using pulsed current (PC1-4ms) at an average current density of 3 A/dm².
Figure 7.38 Surface morphology of pure tin coatings with varying thickness from 0.5 to 5µm.
Figure 7.39  Surface morphology of tin-cobalt alloy multilayer coatings with varying thickness of tin-cobalt alloy sublayers. These sublayers were deposited using pulsed current (PC1-4ms) at an average current density of 3 A/dm$^2$, whilst pure tin sublayers were deposited using direct current at 0.5 A/dm$^2$. 
Figure 7.40 Effect of thickness on the surface morphology of single layer tin-cobalt alloy coatings. These sublayers were deposited using pulsed current (PC1-4ms) at an average current density of 3 A/dm².
Figure 7.41 Surface morphology of tin-cobalt alloy multilayer coatings with tin-cobalt alloy sublayers deposited by different current waveforms
**Figure 7.42** Optical cross-sectional micrographs showing the multilayered structure of Sn-Co/Sn CMM coatings. The thickness of the Sn-Co alloy layers (bright layers) was maintained at 1 μm, whilst the thickness of the pure tin layers (dark layers) was varied from 1 μm (a), 2 μm (b), to 3 μm (c). The overall thickness of the CMM coatings was approximately 12 μm.
Figure 7.43 Cross-section of a Sn-Co/Sn multilayer coating on copper substrate. Each of the individual layers was designed to be 0.5 μm. There are 26 layers in total. The coating was protected by a copper electrodeposit (about 5 μm) to avoid damage during sample preparation.

Figure 7.44 Cross-section of a Sn-Co/Sn multilayer coating deposited on the surface of a plain bearing as an overlay. The thickness of Sn-Co alloy layers and tin layers was designed to be 1 and 2 μm, respectively.
Figure 7.45 Cross-section micrograph showing the location of elemental mapping trials. The bright layers are tin-cobalt alloy, whilst the grey layers which have been etched more heavily are mainly tin.
Figure 7.46 Elemental mapping showing the composition modulation in a tin-cobalt alloy multilayer coating on the surface of an aluminium alloy plain bearing plated with a nickel barrier.
Figure 7.47 Micrographs showing the formation of fatigue pits (a) and a loose piece of overlay still held in place (b). The plain bearing overlay has failed by fatigue cracking at 90 MPa.
Figure 7.48 Typical morphology of fatigue trenches. The fatigue strength of the multilayer coating was 83MPa
Figure 7.49  SEM examination of the bottom of a fatigue pit

(a) the overview of the examined fatigue pit

(b) Areas like A in (a), showing a crystalline morphology

(c) Areas like B in (a), showing a rough morphology
Figure 7.50  Cross-section of a plain bearing after fatigue testing. Fatigue strength: 90 MPa. Thickness configuration: 1 µm Sn-Co alloy layers and 2 µm tin layers.

(a) A fatigue crack stopped at the interface on reaching the hard alloy layer  
(b) Fatigue pits with/without steps on the walls  
(c) Areas without fatigue cracks
Figure 7.51  Micrograph showing the propagation of fatigue cracks in a multilayer overlay with a fatigue strength of 69 MPa. Note how the crack propagates along a sublayer.
Figure 7.52 Variation of the deflection of the extended copper wire with the progress of deposition of single layer tin-cobalt alloy coatings.

(a) 20% cobalt metal in the solution, PC1-4ms, \( i_a = 3 \text{ A/dm}^2 \)

(b) 20% cobalt metal in the solution, DC, \( i = 3 \text{ A/dm}^2 \)

(c) 15% cobalt metal in the solution, PC1-4ms, \( i_a = 3 \text{ A/dm}^2 \)

(d) 15% cobalt metal in the solution, DC, \( i = 3 \text{ A/dm}^2 \)
Figure 7.53 Development of internal stress in tin-cobalt alloy multilayer coatings obtained from the solution containing: (a) 15% cobalt as metal, (b) 20% cobalt as metal
FIGURE 7.54 Effect of current waveform on the internal stress in deposits obtained from the solution containing 15% cobalt as metal.

(Note that the negative sign of the stress values represents a compressive internal stress)
Figure 7.56  Dependence of internal stress on the sublayer thickness in multilayer coatings from the solution containing 15% cobalt as metal. (Note that the negative sign of the stress values represents a compressive internal stress)

Figure 7.57  Dependence of internal stress on the sublayer thickness in multilayer coatings from the solution containing 20% cobalt as metal. (a) constant thickness (1 μm) of tin-cobalt alloy sublayers; (b) equal thickness of tin and tin-cobalt alloy sublayers; (c) constant thickness (1 μm) of tin sublayers. (Note that positive stress values represent a tensile internal stress)
Figure 7.58 Effect of frequency on the internal stress in deposits from a solution containing 15% cobalt as metal.

Figure 7.59 Development of internal stress with deposition time in single layer tin-cobalt alloy deposits obtained at different frequencies. The pulsed current employed had a duty cycle of 33%.
Figure 7.60 Effect of Tween 20 on the internal stress in coatings deposited from a solution containing 15% cobalt as metal under direct current conditions. Negative stress values indicate that the internal stresses are compressive.

Figure 7.61 Effect of Tween 20 on the compressive internal stress in coatings deposited from a solution containing 15% cobalt as metal under pulsed current conditions (PCI-2ms). The average current density applied was 3 A/dm².
Figure 7.62 Effect of Tween 20 on the cathodic potentiodynamic polarisation curves for the deposition of tin from a solution containing 36g/l SnSO$_4$, 120g/l sodium gluconate, 30g/l H$_3$BO$_3$, 20g/l Na$_2$SO$_4$·10H$_2$O, pH 4, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.63 Effect of Tween 20 on the cathodic potentiodynamic polarisation curves for the deposition of cobalt from a solution containing 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, pH 4, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.64  Relationship between the cathodic potentiodynamic polarisation curves for the deposition of (a) tin from a solution containing 36g/l SnSO$_4$, (b) cobalt from a solution containing 24g/l CoSO$_4$·7H$_2$O, and (c) tin-cobalt alloys from a solution containing 36g/l SnSO$_4$ and 24g/l CoSO$_4$·7H$_2$O. All the solutions also contained 120g/l sodium gluconate, 30g/l H$_3$BO$_3$, 20g/l Na$_2$SO$_4$·10H$_2$O, pH 4, Temperature 45-50°C.
Figure 7.65 Effect of Tween 20 on the potentiodynamic polarisation curves for the deposition of tin-cobalt alloys from a solution containing 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, pH 4, Temperature 45-50°C.
Figure 7.66 Effect of potential sweep rate on the cathodic polarisation curves for the deposition of tin-cobalt alloys from a solution containing 36g/l SnSO$_4$, 24g/l CoSO$_4$·7H$_2$O, 120g/l sodium gluconate, 30g/l H$_3$BO$_3$, 20g/l Na$_2$SO$_4$·10H$_2$O, 4ml/l Tween 20, pH 4, Temperature 45-50°C.
Figure 7.67  Time responses of the cathode under different constant potentials in a solution for tin-cobalt alloy deposition. The solution consisted of 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, 4ml/l Tween 20, pH 4, Temperature 45-50°C.
Figure 7.68 Cathodic polarisation curves obtained by different potential sweep methods for the deposition of tin-cobalt alloys from a solution containing 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, 4ml/l Tween 20, pH 4, Temperature 45-50°C. The composition of deposits obtained at different constant potentials is also presented.
Figure 7.69 Cathodic potentiodynamic polarisation curves for the deposition of tin-cobalt alloy on different substrates from a solution containing 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, 4ml/l Tween 20, pH 4, Temperature 45-50°C. Potential sweep rate 2mV/s.
Figure 7.70 Potentiodynamic polarisation curve for the deposition of tin-cobalt alloys from a solution containing 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, 4ml/l Tween 20, pH 4, Temperature 45-50°C. The working electrode potential was swept from -1700 mV to -100 mV at a sweep rate of 2 mV/s.
Figure 7.71 Effect of agitation on the cathodic polarisation curves for the deposition of tin-cobalt alloy from the solution without addition of Tween 20. Potential sweep rate 2mV/s.
Figure 7.72 Effect of agitation on the cathodic polarisation curves for the deposition of tin-cobalt alloys from the solution with the addition of 4 ml/l Tween 20. Potential sweep rate 2mV/s.
Figure 7.73: Effect of agitation level on the cathodic polarization curves for the deposition of tin from the solution by without the addition of 4% Tween 20

Figure 7.73 (a)
**Figure 7.73** Effect of agitation level on the cathodic polarisation curves for the deposition of tin from the solution

(a) without the addition of Tween 20

(b) with the addition of 4ml/l Tween 20
Figure 7.74 Effect of agitation on the cathodic polarisation curves for the deposition of cobalt from the solution with the addition of 4 ml/l Tween 20. Potential sweep rate 2mV/s.
Figure 7.75 Effect of tin(II) sulphate on the cathodic polarisation curves for the deposition of tin-cobalt alloys. The solution also contained 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, pH 4, Temperature 45-50°C.
Figure 7.76 Effect of cobalt sulphate on the cathodic polarisation curves for the deposition of tin-cobalt alloys. The solution also contained 36g/l SnSO₄, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, pH 4, Temperature 45-50°C.
Figure 7.77 Cathodic potentiodynamic polarisation curves for the deposition of tin-cobalt alloys from solutions containing different cobalt contents as metal. All of these solutions contained 120g/l sodium gluconate, 30g/l H$_3$BO$_3$, 20g/l Na$_2$SO$_4$·10H$_2$O, and 4ml/l Tween 20, pH 4, Temperature 45-50°C. Potential sweep rate 2mV/s.
Figure 7.78 Effect of pH on the cathodic polarisation curves for the deposition of tin from a solution containing 36g/l SnSO₄, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, Temperature 45-50°C. Open circuit potential -100 to -300 mV vs. SCE. Sweep rate 2mV/s.
Figure 7.79 Effect of pH on the cathodic polarisation curves for the deposition of cobalt from a solution containing 24g/l CoSO₄, 7H₂O, 120g/l sodium gluconate, 30g/l KClO₃, 20g/l Na₂SO₄, 10H₂O. Temperature 45-50°C. Potential sweep rate 2mV/s.
Figure 7.80 Effect of pH on the cathodic polarisation curves for the deposition of tin-cobalt alloys from a solution containing 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.81 Effect of pH on the cathodic polarisation curves for the deposition of tin-cobalt alloys from a solution containing 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, 4ml/l Tween 20, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.82 Effect of the concentration of sodium gluconate on the cathodic polarisation curves for the deposition of tin. The solution also contained 36g/l SnSO₄, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, pH 4.0, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.83 Effect of the concentration of sodium gluconate on the cathodic polarisation curves for the deposition of cobalt. The solution also contained 24g/l CoSO$_4$·7H$_2$O, 30g/l H$_3$BO$_3$, 20g/l Na$_2$SO$_4$·10H$_2$O, pH 4.0, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.84 Effect of the concentration of sodium gluconate on the cathodic polarisation curves for the deposition of tin-cobalt alloys. The solution also contained 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 30g/l H₃BO₃, 20g/l Na₂SO₄·10H₂O, pH 4.0, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.85 Effect of boric acid on the cathodic polarisation curves for the deposition of tin-cobalt alloys. The solution also contained 36g/l SnSO$_4$, 24g/l CoSO$_4$$\cdot$7H$_2$O, 120g/l sodium gluconate, 20g/l Na$_2$SO$_4$$\cdot$10H$_2$O, pH 4.0, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.86 Effect of boric acid on the cathodic polarisation curves for the deposition of tin-cobalt alloys. The solution also contained 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 20g/l Na₂SO₄·10H₂O, 4ml/l Tween 20, pH 4.0, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.87 Comparison of the cathodic polarisation curves of fresh and aged solutions for the deposition of tin-cobalt alloys, with/without the addition of 4ml/l Tween 20. Potential sweep rate 2 mV/s.
Figure 7.88 Anodic polarisation curve of a tin-cobalt alloy deposit in the plating electrolyte containing 36g/l SnSO₄, 24g/l CoSO₄·7H₂O, 120g/l sodium gluconate, 20g/l Na₂SO₄·10H₂O, 4ml/l Tween 20, pH 4.0, Temperature 45-50°C. Potential sweep rate 2 mV/s.
Figure 7.89 Variation of pH value with the addition of 2.5 M sodium hydroxide to tin-cobalt alloy electrolytes of different cobalt concentrations. The open data-points indicate the pH value at which precipitation takes place.
Figure 7.90 Variation of the pH value with the addition of 2.5 M sodium hydroxide to solutions containing different concentrations of tin(II) sulphate and 120 g/l sodium gluconate and 30 g/l boric acid. The open data-points indicate the pH value at which precipitation takes place.

Figure 7.91 Variation of the pH value with addition of 2.5 M sodium hydroxide to solutions containing 24 g/l cobalt sulphate and other bath constituents, including 120 g/l sodium gluconate, 30 g/l boric acid, and 20 g/l sodium sulphate
Figure 7.92 Variation of pH value with the addition of 2.5 M sodium hydroxide to tin-cobalt alloy electrolyte containing different concentrations of boric acid. The open data-points indicate the pH value at which precipitation takes place.

FIGURE 7.93 Variation of pH value with the addition of 2.5 M sodium hydroxide to solutions containing different concentrations of sodium gluconate and 12 g/l tin(II) sulphate, 30 g/l boric acid. The open data-points indicate the pH value at which precipitation takes place.
Figure 7.94 AES depth profiles of two tin-cobalt alloy deposits deposited at 2 A/dm² using direct current. After electrodeposition, the deposit was (a) immediately removed from the solution, (b) immersed in the solution for another 30 minutes.
Figure 7.95 Sections of X-ray diffraction patterns for tin-cobalt alloys obtained under different plating conditions.
**Figure 7.96** Mass transport model for pulse plating following Ibl [74]

**Figure 7.97** Relationship between the dimensionless transition time $r^*$ and the dimensionless peak current density $j_p^*$ at different duty cycles
Figure 7.98 Schematic illustration of the dependence of the actual metal deposition rate on the plating time under different peak current densities. The actual metal deposition rate decreases after the plating time is longer than the corresponding transition time. 

\[ T_{on} = \tau > \tau_1 > \tau_2 > \tau_3 \]
Figure 7.99 Schematic illustration of the dependence of the average current density for metal deposition on the applied peak current density at a given duty cycle and frequency.
Figure 7.100 The relationship between the average current density for metal deposition and the applied peak current densities under different frequencies. $f_0$ and $f_\infty$ represent very low and very high frequencies, respectively.
Figure 7.101 Dependence of \( \frac{j_{pt}}{j_{lim}} \) on duty cycle \( \theta \) at constant on-times.
Figure 7.102 Schematic illustration of the predicted tendency for the variation in deposit composition with frequency at different peak/average current densities. The duty cycle is assumed to be 50%.