Microstructural and Mechanical Assessment of Pulse-Reverse Plated Cobalt Matrix Nanocomposite Coatings

Thesis submitted for the degree of Doctor of Philosophy At the University of Leicester

By Dhuha F. Albusalih Department of Engineering University of Leicester 2018



ABSTRACT

Microstructural and Mechanical Assessment of Pulse-Reverse Plated Cobalt Matrix Nanocomposite Coatings

Dhuha Albusalih University of Leicester, 2018

Electrodeposited metal matrix nanocomposites (MMNCs) offer improved mechanical properties for tribological coatings. The development of nanotechnology in the last 25 years means there are now a multitude of nanoparticles, nanowires and nano-tubes available in an ever- increasing range of materials and hence the scope for new nanocopmosites coatings by electrodeposition is greater than ever, with the potential to develop a coating with functional performance equivalent to hard chrome.

Recent work on pulse reverse deposition of MMNCs by Weston, et al has suggested the capability to control the co-deposition of metals and particulates. The technique includes the use of a surfactant and pulse reverse plating (PRP). In the present work, the suggested mechanism investigated on cobalt matrix nanocomposites with a number of particles including SiC, Al₂O₃, and PTFE with different particles loading and size. The produced nanocomposites assessed microstructurally and mechanically by different analysis: Field emission gun scanning electron microscopy FEGSEM cross section and surface topography, Energy Disperse X-ray EDX, image analysis, X-ray diffraction XRD, and transmission electron microscopy TEM. The microstructural results indicated the applicability of PRP for Co-SiC with different particle loadings, and for Co-SiC with 5 g l⁻¹ Al₂O₃. The mechanical properties of the produced coatings suggests an increase in microhardness with increasing the particles volume fraction with 8.7 vol. % of SiC increasing the hardness by up to 25 % and 9.1 vol% of Al₂O₃ raising it by up to 31 % beyond the hardness of the pure Co coatings.

No significant effect attributed to the reduction of the grain size was observed. A predictive model for the main controlling strengthening (dispersion strengthening) of the nanocomposites with low surfactant content 0.2 g l⁻¹ of SDS was found. The model is applicable on both nanocomposites electroplated cobalt coatings Co-Al₂O₃ and Co-SiC.

PUBLICATIONS

Conferences

- Poster: Durham University for the 21st meeting of the ELECTROCHEM conference series, 13th-15th September 2015, The Mountjoy Centre, Maple Wing, Stockton Road, Durham ,DH1 3LE: Hardness of Electrodeposited Nanocomposites by Pulse Reverse Plating Technique.
- Talk: Leicester University for the 21st meeting of the ELECTROCHEM conference series, 17th-19th August 2016, Stamford Court, Manor Rd, Leicester LE2 2LH.: Electroplated nanocomposites produced by pulse reverse plating (PRP) technique.
- Talk: Leeds university, TRIBOUK, 14th -15th April 2016, School of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT Leeds: Tribological performance of the electroplated nanocomposites (Co-SiC) by Pulse Reverse Plating (PRP).

STATEMENT

All the work described in this thesis for the degree of Ph.D. entitled "Microstructural and mechanical assessment of pulse-reverse plated cobalt matrix nanocomposite coatings" was conducted by the author in the Department of Engineering at the University of Leicester mainly during the period between July 2014 and June 2018.

The work in this thesis is original unless otherwise acknowledged in the text or by references and none of the work has been submitted for another degree at this or any other university.

ACKNOWLEDGEMENT

I would like to thank my supervisory team: Dr. Simon Gill, and Dr. David Weston for all the support, guidance, patience, encouragement, knowledge, and concern to achieve a desirable work that helped me to finish this study. I also would like to thank all the members in mechanics of materials laboratory: Graham Clark, Vinay Patel, Alex Frost, and Ruth Chantry for the all the help in training to conduct most of characterisations with FEGSEM, FIB milling, TEM, nanoindentation and also for their cooperation during my lab work. I would like to express my gratitude to the people in the workshop to provide all the needed help, particularly Tony Forryan for all help to set up my experiments tools and for the joyful chats that we had during the work.

I'm thankful to Cheryl Haidon from Geology department at the University of Leicester for all the assistance in XRD analysis. My colleague Dr. Emily Jane Watkinson from space group for the helpful discussion and help in XRD work.

Many thanks to Dr Rob Thornton for all advice presented during this work and for his help to conduct the wear test at the University of Sheffield. I would like to present my acknowledgements for the mechanics laboratory at the University of Sheffield: the PhD students Marcello Cadeddu and Paulo Herrera for all the assistance and efforts made to help conducting the wear test.

I would like to express my thanks to Professor Andy Cobley and Professor Karl Ryder for their advice in this work. My gratitude to all the people in materials centre/ Chemistry department/ university of Leicester for creating a comfortable environment that helped me to carry on my experiments. I also would like to express my heartfelt gratitude to the mechanics of materials group and my dear friends Dr. Kevser Sevim, Dr. Amnani Binti, Ramy Mesalam, Dr. Mazin AL-Isawy, Basim AL-Bhadle, Rafat Alazzawi, Peter Polak, Dr. Muhanad AL-Sabbagh, Dr. Reza Baserinia, Dr. Baber Saleem, Fikret Yildirim, Dr. Nawshin Dastagir, and Mahmoud Ehnesh, for all the help, sharing experience and for building a lovely atmosphere that ease the work throughout the whole PhD study. I would like to extend my thanks to my friends Nagham Shiltagh and Alaa AL-Taie for being supportive during my study. My endless appreciation and gratitude to my lovely family: my great dad Falah Albusalih and lovely mum Nidaa AL-Eddrissy, all family members: Dina, Saba, Ahmed, Noor, Wathiq, Amir, Ameer, and Sima for pushing me forward during the very difficult time in this journey. My thanks to my family in the UK Dr. Dhia AL-Edrissy and Dr. Nimaat AL-Madaany for their support. Many thanks to my lovely, little guardian angel Abdullah who's always motivates me to have a better future.

Finally, I would like to thank my sponsor, the ministry of higher education and scientific research for funding this project and providing the opportunity to have this experience.

Dhuha June, 2018

DEDICATION

I dedicate this thesis to the memory of my granddad and to my family...

LIST OF TABLES

Table 2-1: Examples of the theoretical models used for the electrodeposition of composites	3
containing particles [15]	13
Table 2-2: Plating parameters of Ni with nano carbon fibre from a previous study [64]	26
Table 4-1: Chemicals used with suppliers	46
Table 4-2: (Co-SiC) Bath composition	47
Table 4-3 Nano (SiC) particle loading-size in Co-SiC	47
Table 4-4: Co-Al ₂ O ₃ and Co-PTFE	48
Table 4-5: Electroplating parameters	51
Table 4-6: Required input for nanoindentation test	66
Table 5-1: EDX analysis for Co-SiC with 5g.l ⁻¹ SiC	79
Table 5-2 : Instrumental line broadening, Values obtained after stripping K α 2	83
Table 5-3: Calculated deposited mass and cathode efficiency of all Co-SiC with different	
particles loading in cobalt bath	99
Table 6-1: Average thickness calculated from FEGSEM images	109
Table 6-2: Calculated Vol. % of the Co-Al ₂ O ₃ coatings with and without oxygen	114
Table 6-3: Void % sub-coat from image analysis	118
Table 6-4: Coatings thickness calculated from the deposited mass	120
Table 6-5: Instrumental line broadening, values obtained after stripping Kα2	126
Table 7-1: EDX analysis showing the chemical composition of coatings from bath 4 for Co)-
PTFE showing high particle content and no clear trend	139
Table 7-2: Calculated Vol. % of the Co-PTFE coatings shows high PTFE particle content,	while
few particle can be seen in FEGSEM images	139
Table 7-3: Image analysis results for bath B4 coatings shows low particle content similarly	' to
the FEGSEM images analysis	140
Table 9-1: Mechanical parameters of Co and Co-SiC coatings showed the resistance to pla	stic
deformation of both coatings with 100 mN loading and for different tc considering the star	ndard
deviation of the nanoindentation tests SSD	166
Table 9-2: Coatings roughness, volume loss and Coefficient Of Friction (COF) for Co, and	l Co-
SiC	169
Table 9-3: Comparison of the wear results from the current work with the earlier studies	170

LIST OF FIGURES

Figure 2-1:Schematic diagram of the basic electrochemical cell7
Figure 2-2: The model for the deposition of Cu-Al ₂ O ₃ coatings described by (Walsh et al,
2014)[19]
Figure 2-3: Diagram showing the input variables that should be considered to model the co-
deposition of nanoparticle into metal matrix and the output results that can be obtained, the
diagram is taken from a review paper by Walsh and Leon, 2014 [19] 10
Figure 2-4: Bubble growth and implosion in a liquid irradiated with ultrasound [50] 19
Figure 2-5: Model of the nanoparticle WS ₂ behaviour into Co matrix taken from a previous
study [16] : (i) from cobalt bath with CTAB surfactant, (ii) from cobalt bath with SDS
surfactant
Figure 2-6: Typical waveform under i) DC and ii) Pulse reverse current
Figure 2-7: Model for behaviour of particles during PRP plating in the cobalt bath with SDS . 28
Figure 3-1: obstacles bowing in Orowan strengthening (Gladman, 1997)
Figure 3-2: The critical radius for the precipitation hardening by the second phase particles [74]
Solid solution strengthening
Figure 3-3: Assumed geometry of GNDs below the indenter
Figure 4-1: Schematic chart explaining the experimental work implemented in this research
considering the plating parameters in similar way according to the literature [19] 44
Figure 4-2: Co-SiC with 0.2 g l^{-1} SDS vol. % against cathodic time, t_c produced from an earlier
work by Weston[78]
Figure 4-3: Electrochemical cell setting with 500 ml bath, and 52 mm spacing between the
counter and the working electrodes that mentioned in details in appendix I
Figure 4-4: Procedure for close up analysis of bath B- 3a and 4-coatings, showing:
Figure 4-5: FIB milling of a specimen of a Co-SiC sample in sequence: (i) the selected area of
the specimen; (ii) two rectangular trenches with the deposited Pt at the top of the specimen; (iii)
extracting the specimen by welding it to the W needle; and (iv) attaching the sample to the Cu
TEM grid in preparation for thinning
Figure 4-6: geometry used for the simplified derivation of Bragg equation
Figure 4-7: Deconvolution of Ka2 from single diffraction peak [96] 60
Figure 4-8: Sample preparation with XRD sample holder for XRD analysis
Figure 4-9: Knoop indenter geometry and the resultant indentation in the workpiece
Figure 4-10: Schematic of Knoop indentations for the plated specimens
Figure 4-11: A schematic for load- displacement in nanoindentation

Figure 4-12: A schematic represent a section through the nanoindentation, (Oliver and Pharr, 1992)
Figure 4-13: Schematic image of the Bruker Universal Mechanical Tester (UMT) with the
rotary drive (shown on the right) used for wear test performance (Ivanov et al, 2012)
Figure 5-1: Volume fraction % variation of the nanocomposites (Co-SiC) accounting for the
effect of SDS content and cathodic time taken from previous data [78]
Figure 5-2: Cross sectional back-scattered images of Co-SiC electrodeposited nanocomposite at
different magnifications from preliminary work [78]72
Figure 5-3: Microhardness of the nanocomposites Co-SiC against the SiC vol.% from the
previous work [78]73
Figure 5-4: Coatings with poor coating- steel adhesion at low duty cycle: i) Co-SiC with $t_c=30$ s, ii) Co-SiC with $t_c=60$ s
Figure 5-5: SEM -BSE cross section of Co-SiC with 5 g l ⁻¹ nano-SiC showing adhesion of the
coatings to the substrate for low and high magnification for coatings with different <i>tc</i> with low
and high magnification for each duty cycle: i) $tc = 60$ s, ii) $tc = 90$ s, iii) $tc = 120$ s, iv) DC with
low magnification, v) DC with higher magnification showing less particle content compare to
the PRP77
Figure 5-6 SiC content of Co-SiC nanocomposite coatings produced by PRP with different duty
cycles, with fixed <i>ta</i> and variable <i>tc</i>
Figure 5-7: SEM images of coatings from bath 2 with 5 g. l ⁻¹ SiC and different duty cycles, i: 1,
ii: 0.71, iii: 0.81, iv: 0.86
Figure 5-8 XRD pattern for pure Co with different cathodic time
Figure 5-9: XRD pattern for Co-SiC with different cathodic times
Figure 5-10: Grain size of pure Co, Co in Co-SiC with different duty cycles in (100) plane
estimated using Scherer equation
Figure 5-11: Grain size estimated using Scherer equation for Co, Co matrix in Co-SiC
nanocomposite in 110 plane with 5 g l ⁻¹ SiC loading and with different duty cycles
Figure 5-12: Grain size variation of Co matrix with SiC vol. % for Co-SiC 5 g l ⁻¹ SiC in (100)
and (110) planes
Figure 5-13: TEM image of spherical nano β -SiC particles from an earlier work, (Heidari, et al,
1992)
Figure 5-14: SiC nanoparticles dispersion with some agglomeration in i and ii
Figure 5-15: Bright-field, cross-sectional TEM image: i) A DC-plated Cu–Al ₂ O ₃ composite on
a rotating disk electrode with a wide particle size distribution, ii) A PRC-plated Cu-Al ₂ O ₃
nanocomposite onto a rotating disk electrode showing Al ₂ O ₃ nanoparticles dispersion with
particles of 100 nm [7, 125]

Figure 5-16: Highlighted SiC nanoparticles with uniform dispersion through Co with
highlighted nanoparticles and measured spacing between particles
Figure 5-17: Electroplated Co and Co-SiC produced in an earlier and current work showing Co
grains and grain boundries i) TEM image of electroplated Co produced by DC, [126], grain size
400-500 nm, ii) TEM image of Co-SiC in this work PRP, tc= 60 s, Grain size 35-100 nm 89
Figure 5-18 Comparison of i) original TEM image with grains boundaries of Co matrix with, ii)
Schematic representation of Co grains boundaries
Figure 5-19: SiC nanoparticles with diameter = 32.3 nm dispersed within the grain of Co matrix
as measured in TEM and without agglomeration
Figure 5-20: BSE images SEM, high magnification cross section of the Co-SiC, $t_c = 60$ s with
different loadings at two different magnifications: i) 5 g l ⁻¹ , ii) 10 g l ⁻¹ , iii) 15 g l ⁻¹ , iv) 20 g l ⁻¹ , v) 25 g l ⁻¹
Figure 5-21: SiC volume fraction (%) calculated from EDX with different tc for Co-SiC with
0.2 g l ⁻¹ SiC: i) 5 g l ⁻¹ , ii) 10 g l ⁻¹ , iii) 15 g l ⁻¹ , iv) 20 g l ⁻¹ , v) 25 g l ⁻¹
Figure 5-22: XRD pattern of Co-SiC at tc = 60s with different particle loadings of 5-25 g l ⁻¹ SiC
Figure 5-23: Crystallite size distribution of cobalt matrix with different particles vol.%
with different SiC loadings compared to Co WS, from an earlier work by Wester, at al [16], 00
with different SiC loadings compared to Co-wS ₂ from an earlier work by weston, et al [16]99
Figure 5-25: Cathodic efficiency of coatings with different particle loadings for different
cathodic times with the consideration of the dissolution of Co
Figure 5-26: A plot of Co-SiC electrodeposits grain size against volume fraction of the SiC
and size 50 nm
Figure 6-1: FEG-SEM cross-section images of coatings from bath 3a-PRP with different tc: i)
30s with highlighted dissolution at the interface area between the coating and the substrate as
well as some extended microcracks to the coating , ii) 60s, iii) 90s, iv) DC 105
Figure 6-2: BSE image of Co-Al ₂ O ₃ from bath 3-a with 0.0 g l^{-1} SDS, presenting particles
dispersion through the cross-sections for different tc:
Figure 6-3: BSE image of Co-Al ₂ O ₃ from bath 3-a, and b (with 0 g l^{-1} SDS and 0.2 g l^{-1} SDS)
with t_c : i) 30 s, ii) 90 s iii) 120 s and 0.2 g 1^{-1} SDS and tc = iv) 30 s, v) 90 s vi) 120 s
respectively
Figure 6-4: FEGSEM cross-section images of coatings from bath 3-PRP with $tc = 60$ s with the
effect of SDS addition: i) 0.2 g l ⁻¹ , ii) 0.4 g l ⁻¹ , iii) 0.6 g l ⁻¹ , iv) 0.8 g l ⁻¹
Figure 6-5: Co-Al ₂ O ₃ coatings cross section thickness against the cathodic time for the different
SDS content

Figure 6-6: Topography FEGSEM of: i) 3b-30 s with spread voids through the coatings surface,
ii) 3-b-60 s cobalt matric particles with alumina particles imbedded, iii) No big change in Co
matrix grain size with $t_c=90$ s, iv) 3b- DC
Figure 6-7: Alumina vol. % in Co-Al ₂ O ₃ against SDS concentration of Co-Al ₂ O ₃ produced by
DC
Figure 6-8: Volume fraction of Al ₂ O ₃ against cathodic time <i>tc</i> for coatings from bath 3a-e with
different SDS concentration
Figure 6-9: EDX analysis represented by volume fraction of Al ₂ O ₃ nanoparticles with different
SDS surfactant content
Figure 6-10: the voids formed in coating and substrate
Figure 6-11: Cathode current efficiency of Co-Al ₂ O ₃ calculated from the measured thickness
against cathodic time t _c
Figure 6-12: Cathode current efficiency of Co-Al ₂ O ₃ calculated from the measured mass against
cathodic time <i>tc</i>
Figure 6-13: Cathode current efficiency of Co-Al ₂ O ₃ against SDS concentration
Figure 6-14: XRD pattern for Co-Al ₂ O ₃ , from B3-b and different cathodic time t _c 125
Figure 6-15: XRD pattern for Co-Al ₂ O ₃ , $tc = 60$ s with different SDS concentrations
Figure 6-16: Grain size distribution of cobalt matrix in 100 with different Al ₂ O ₃ particles vol.%
Figure 6-17: Grain size distribution of cobalt matrix in110 with different Al ₂ O ₃ particles vol.%
Figure 6-18: Volume fraction of the alumina nanoparticles plotted against the normalised
deposited cobalt thickness to the particle diameter per cycle for different SDS content and tc 129
Figure 6-19: Volume fraction of the alumina nanoparticles plotted against the normalised
deposited cobalt thickness to the particle diameter per cycle in this study compared to the
previous study by Weston [16] for 0.2 g $l^{\text{-}1}$ SDS and different t_{c} 129
Figure 6-20: Surface coverage of alumina particle fraction per cycle against the cobalt deposited
per cycle in PRP with different SDS concentration in the bath
Figure 6-21: Surface coverage of SiC nanoparticles fraction per cycle
Figure 6-22: Co-Al ₂ O ₃ grain size against volume fraction of particles for different SDS contents
Figure 7-1: BSE images of bath 4 and 0.2 g l^{-1} SDS for Co-PTFE cross section: i) $t_c=30$ s, ii)
t _c =60 s
Figure 7-2: Topography of PRP and DC coatings from bath 4b with 0.2gl ⁻¹ SDS: i) tc=60 s, and
ii) DC

Figure 7-3: EDX analysis of a selected coating of Co-PTFE showing the peak overlap of Co and			
F:i) The selected area for the analysis of the coating cross section with high magnification, ii) chemical composition of the elements, and iii) EDX spectra			
work			
Figure 7-5: XRD patterns for Co-PTFE coatings of t_c = 60 s and different SDS content, the			
analysis performed using pure Si			
Figure 7-6 XRD analysis of the Co-PTFE coatings produced from bathB4-b with different duty			
cycle			
Figure 8-1: Knoop microhardness against pure Co coatings and nanocomposite Co-SiC coatings			
with a bath loading of 5 g l ⁻¹ SiC and 50 nm diameter particles			
Figure 8-2: Microhardness of Co-SiC coatings from baths of different loadings of SiC content			
5-15 g l ⁻¹ against volume fraction of SiC nanoparticles			
Figure 8-3: Microhardness of Co-nano SiC against crystallite size distributed in (100) direction.			
Figure 8-4: Microhardness of Co-nano SiC against crystallite size distributed in (110) direction			
$\mathbf{F}_{\mathbf{r}} = 0 5 \mathbf{I} \mathbf{I} \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} r$			
Figure 8-5: Least squares fit of equation (8.1) to hardness data for Co and Co-SiC coatings as a $1/1$			
function of inverse particle spacing, $1/Lp$, and inverse root grain size, $1/d$, (a) 3D view, (b) 2D			
aspect showing effect of grain size, (c) 2D aspect showing effect of particle spacing			
Figure 8-6: Microhardness of Co-Al ₂ O ₃ coatings from baths with 0-0.4 g l^{-1} SDS content and			
tc = 60-120 s against value fraction of 45 nm diameter nanoparticles			
Figure 8-7: Microhardness of Co-Al ₂ O ₃ against grain size distributed in (100) direction 153			
Figure 8-8: Microhardness of Co-Al ₂ O ₃ against grain size distributed in (110) direction 154			
Figure 8-9 :Least squares fit of equation (8.2) to hardness data for Co and Co- Al_2O_3 coatings as			
a function of inverse particle spacing, $1/Lp$, and inverse root grain size, $1/d$, (a) 3D view, (b)			
2D aspect showing effect of grain size, (c) 2D aspect showing effect of particle spacing 156			
Figure 8-10: Micro indentation and nanoindentation measurements for the Knoop hardness of			
pure cobalt and Co-SiC for different cathodic times 60-3600 s 159			
Figure 8-11: micrograph of (i) Knoop and (ii) Berkovich indentations with 10 g or (mN)			
through the finished coating surface cross section with an average thickness 25 μ m 159			
Figure 8-12: Load-displacement plots for the electroplated Co and Co-SiC nanocomposites with			
the same electroplating conditions			
Figure 8-13 Least square fitting for the Indentation size effect (ISE) data for Co electroplated			
nano-polycrystalline obtained by nanoindentation experiment. The straight line represents the			
linear fitting of all the produced coatings at different loading- indentation depth for the			
nanoindentation			

Figure 8-14 Least square fitting for the Indentation size effect (ISE) data for Co-SiC
electroplated nano-composites. The straight line represents the linear fitting of all the produced
coatings at different loading- indentation depth for the nanoindentation
Figure 8-15: Predicted hardness against particle volume fraction for Co-SiC and Co-Al ₂ O ₃ using
equation (8.4)
Figure 8-16: Predicted hardness against particle volume fraction for Co-SiC and Co-Al ₂ O ₃ using
equation (8.1)
Figure 9-1: Co and Co-SiC predicted wear resistance as a function of H ³ /E ² for selected films of
pure Co and Co-SiC with different cathodic time plating parameter. E is the elastic modulus of
Co and Co-SiC measured by nanoindentation test
Figure 9-2: 3D representation of the wear scar and the method used to measure the volume lost
in 3D microscope
Figure 9-3: Wear rate for Co and Co-SiC for different <i>tc</i>
Figure 9-4: Coefficient of friction $COF(\omega)$ for pure cobalt produced by PRP, tc=60s and DC172
Figure 9-5: Coefficient of friction COF (ω) for Co-SiC produced by PRP, tc=60s and DC 172
Figure 9-6: (i, ii, iii, iv): SEM images of the worn surface of Co and Co-SiC
Figure 9-7: EDX analysis for the chemical composition of the worn surface of Co-SiC, $t_c = 60$ s
Figure 9-8: EDX analysis of the Alumina ball contact surface with the cobalt coatings from
three different positions showed some cobalt at the contact area
Figure 10-1 Predicted hardness against particle volume fraction up to 20 vol. % for Co-SiC and
Co-Al ₂ O ₃ using equation (8.4)
Figure 10-2 Predicted hardness for both nanocomposites of Co-SiC and Co-Al ₂ O ₃ using
equation (8.5)

LIST OF ACRONYMS

BSE	Back scattered electron
CAE	Constant analyser energy
CE	Counter electrode
CTAB CV	Cetrimonium bromide Cyclic voltammetry
DC EDX	Direct current Energy-dispersive X-ray spectroscopy
ЕНС	Electroplated engineering hard chromium
EPD	Electrophoretic deposition
FIB	Focus ion beam
FWHM	Full width at half maxima
GNDs	Geometry needed dislocations
НК	Hardness Knoop
IFM	Infinite focus microscopy
ISE	Indentation size effect
KHN	Knoop hardness number
NIST	National institute of standards
PRP	Pulse reverse plating
PRC	pulse reverse current
PTFE	Polytetrafluoroethylene
RE	Reference electrode

SDS	Sodium dodecylsulfate
SE	Secondary electron
SEM	Scanning electron microscopy
SSD	Standard error
TEM	Transmission electron microscopy
US	Ultrasonic system
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbol	Description	Unit
Z	Valence number of metal	
F	Faraday constant=964500	$C \text{ mol}^{-1}$
$p_{\rm m}$	Deposited metal density	kgm ⁻³
M_{m}	Atomic weight of the deposited metal	g. mole ⁻¹
i ₀	Exchange current density	A.cm ⁻²
η	Electrode overpotential	
Cb	bulk concentration of particles	
Ic	Cathodic current	Ampere
Ia	Anodic current	Ampere
tc	Cathodic time	second
ta	Anodic time	second
Qc	Cathodic charge per cycle	Coulombs,
		A.s
Qa	Anodic charge per cycle	Coulombs,
		A.s
As	Surface area of the specimen	m ²
N cycle	Number of cycle	
ti	Time	Second
Vol%	Volume fraction	
at.%	Atomic fraction	

w_i , wt.%	Mass fraction	
rpm	Revolution per minute	rpm
Duty cycle	The real time during the cycle that deposition is	
	effective	
τ	Shear stress	Gpa
μ	Shear modulus	Gpa
b	Burger vector	
$ au_{ m c}$	Critical shear stress	Gpa
Lp	Spacing between precipitates	nm
r _p	The mean precipitate radius	m
f	Precipitate volume fraction	
$ au_{ m s}$	Shear stress of solid solution	N.m ⁻²
n	The number of dislocation line	
V	Volume of the material	m ³
ρ	Dislocation density	1.m ⁻²
$\gamma_{ m P}$	Plastic shear strain	m
$ ho_m$	Mobile dislocation density	1.m ⁻²
- _X	The mean free path of the dislocation	nm
$ ho_{im}$	Immobile dislocation	
d	Grain size	nm
$ ho_{\circ}$	Initial dislocation density	$1.m^{-2}$
L _G	Spacing between grain	nm
L_{F}	Spacing between barrier in forest strengthening	nm
$ au_{y}$	Critical shear stress	Gpa, Mpa
Н	Hardness	N.m ⁻²

h	Depth of indentation	μm, nm
Р	Applied load	Gram,
		Newton
$F_{\rm F}$	Friction coefficient	
λ	Wavelength	A°, Angstrom
θ	Bragg angle	°, degree
β	Sample line broadening	radian
В	The instrumental effect on line broadening	radian
S	Stiffness	N/m
υ	Poison ratio	
ø	The peak broadening angle	Radian
th	Coating thickness	μm
Py	Yield pressure	Gpa
Ra	Surface roughness	μm
COF	Coefficient of friction	

TABLE OF CONTENTS

ABSTRACT		I
PUBLICATIO	NS	II
STATEMENT		III
ACKNOWLEI	DGEMENT	IV
DEDICATION		VI
LIST OF TAB	LES	VII
LIST OF FIGU	RES	VIII
LIST OF ACR	ONYMS	XIV
LIST OF SYM	BOLS	XVI
TABLE OF CO	DNTENTS	XIX
CHAPTER 1	: INTRODUCTION	1
1.1 BA	CKGROUND	1
1.2 AI	MS AND OBJECTIVES	3
1.3 TH	ESIS STRUCTURE	4
CHAPTER 2	• I ITERATURE REVIEW OF ELECTROPI ATING OF NANOCOMPO	SITES
BY DIRECT	CURRENT (DC) PULSE REVERSE PLATING (PRP)	6
2.1 IN	FRODUCTION	6
2.2 EL	ECTRODEPOSITION OF NANOCOMPOSITES	7
2.2.1	Models	
2.3 EF	FECTIVE PARAMETERS AFFECTING THE CO-DEPOSITION OF NANOCOMPOSITES	
2.3.1	Effect of bath composition	
2.3.2	Effect of particle characteristics	
233	Electrolyte parameters	15
L.	Surfactant effect	
II.	Effect of temperature	
III.	Effect of bath agitation	
IV.	Effect of current density	21
2.3.4	Electrodeposition control techniques	22
I.	Co-deposition by direct current (DC):	22
II.	Co-deposition by Pulse Reverse Plating (PRP):	
2.4 Co	-MATRIX NANOCOMPOSITE ELECTRODEPOSITION	29
CHAPTER 3	: LENGTH-SCALE PLASTICITY THEORY AND STRENGTHENING	
MECHANIS	MS OF NANOCOMPOSITES	
3.1 IN	FRODUCTION	31
3.2 IN	FRINSIC LENGTH SCALES	31
3.2.1	Precipitation hardening	32
3.2.2	Forest hardening	35
3.2.3	Grain boundary strengthening	
3.3 Ex	TRINSIC LENGTH SCALES	37
3.3.1	Strain gradient hardening	38
3.4 Co	MBINING LENGTH SCALE EFFECTS	38
3.4.1	Indentation Testing	39
CHAPTER 4	: METHODOLOGY AND EXPERIMENTAL WORK: NANOCOMPOSI	TES

CHAPTER 4: METHODOLOGY AND EXPERIMENTAL WORK: NANOCOMPOSI COATING PREPARATION AND MICROSTRUCTURAL CHARACTERIZATION TECHNIQUES 43

4.1	INTRODUCTION	43
4.2	COATING PRODUCTION	44
4.2.1	Materials	44
I.	Pure Co and Co-SiC system with controlled particle loading and different particle sizes	44
II.	Co-Al ₂ O ₃ and Co-PTFE systems	48
4.2.2	Electrochemical design	49
4.2.3	B Electrochemical cell set up	50
4.3	MICROSTRUCTURAL CHARACTERIZATION WITH ADVANCED ELECTRON MICROSCOPY AND	X-
RAY DI	FRACTION	51
43	Scanning electron microscony (SFM)	
7.J.I I	Sample preparation	
і. П	SEM characterization	
13	Transmission Electron Microscopy (TEM) Imaging	
4.5.2	P. V. Day, Diffugation (VDD)	
4.5.5	Theory of VDD	54 55
l. т	Ineory of XRD	
11.	Crystainte size analysis in AKD	
4.4	MEGUANICAL PROPERTIES CHARACTERIZATION OF THE PRODUCED COATTING	60
4.4	MECHANICAL PROPERTIES CHARACTERIZATION OF THE PRODUCED COATINGS	61
4.4.1	Microhardness indentation	61
4.4.2	P Nanoindentation test	63
I.	Indenter type	65
II.	Test procedure	65
4.4.3	8 Tribological performance	66
I.	Sliding wear test setup	66
II.	Sample preparation and electroplating	67
II	. Test procedure	67
IV	7. Surface characterization	68
СНАРТЕ	R 5: MICROSTRUCTURAL CHARACTERISATION OF CO-SIC	
01111 11		
5.1	INTRODUCTION	70
5.2	RESULTS	74
5.2.1	Microstructural Analysis of Co-SiC and Pure Co coatings with different duty cycles.	74
I.	Field Emission Gun Scanning Electron Microscopy FEG-SEM	74
II.	Energy Disperse X-ray Spectroscopy EDX	78
II	. Surface topography	79
IV	7. X-Ray Diffraction (XRD)	80
V	ТЕМ	86
5.2.2	2 Microstructural analysis of Co-SiC with Different Particle Loadings and Sizes	91
I.	FEG-SEM	91
II.	Energy Disperse X-Ray Spectroscopy	94
II	. XRD	96
5.3	DISCUSSION	97
5.3.1	Mechanism for Co-SiC co-deposition with different particle loadings	97
5.3.2	Effect of SiC volume fraction on crystallite size reduction	101
5.4	CONCLUSION	102
CHAPTE	R 6: NOVEL CO-AL ₂ O ₃ ELECTRODEPOSITED NANOCOMPOSITES	104
6.1	INTRODUCTION	104
6.2	RESULTS	105
62	Field Emission Gun Scanning Electron Microscopy FEGSEM Characterization	105
J.2.1 I	Cross section	105
т. П	Surface topography	 110
621	Fnerov disperse X-Rav FDX Analysis	110 111
6.2.2	Energy usperse A-hay LDA Anarysis	עעע רוי
0.2.3	Image analysis	11/
0.2.4	Deposuea Mass	118
6.2.5	Catnoaic Efficiency	120
6.2.6	• X-Kay Diffraction Analysis	124
6.3	DISCUSSION	127
62	PRP and SDS machanism	177

6.3.2	Effect of particle volume fraction on crystallite size	132
6.4	CONCLUSION	133
CHAPTE	R 7: PRODUCTION OF CO-PTFE COMPOSITES	135
7.1	INTRODUCTION	135
7.2	Results	136
7.2.1	Field emission gun scanning electron microscopy (FEGSEM) Characterization	136
I.	Cross section	136
II.	Surface topography	137
7.2.2	EDX analysis	138
7.2.3	Image analysis	140
7.2.4	Cathode efficiency	140
7.2.5	XRD analysis	141
726	Discussion and Conclusion	143
MECHAN	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT	
MECHAN NANOCO	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES	14 4
MECHAN NANOCO 8.1	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES	144 144
MECHAN NANOCO 8.1 8.2	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES Introduction Results	144 144 144
MECHAN NANOCO 8.1 8.2 8.2.1	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES INTRODUCTION Results Microhardness Indentation	144 144 144 144
MECHAN NANOCO 8.1 8.2 8.2.1 I.	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES INTRODUCTION RESULTS <i>Microhardness Indentation</i> Microhardness of the Pure Cobalt and Co-SiC	144 144 144 <i>144</i> 145
MECHAN NANOCO 8.1 8.2 8.2.1 I.	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES	144 144 144 144 145 145
MECHAN NANOCO 8.1 8.2 8.2.1 I.	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES. INTRODUCTION	144 144 144 144 145 145 149
MECHAN NANOCO 8.1 8.2 8.2.1 I. II.	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES. INTRODUCTION RESULTS Microhardness Indentation Microhardness of the Pure Cobalt and Co-SiC 8.2.1.1.1 Influence of microstructure 8.2.1.1.2 A model of microhardness for nano-composite Co-SiC coatings Co-Al ₂ O ₃	144
MECHAN NANOCO 8.1 8.2 8.2.1 I. II.	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES INTRODUCTION RESULTS <i>Microhardness Indentation</i> Microhardness of the Pure Cobalt and Co-SiC 8.2.1.1.1 Influence of microstructure 8.2.1.1.2 A model of microstructure Co-Al ₂ O ₃ A. Influence of microstructure	2 144 144 144 144 145 145 149 151 151
MECHAN NANOCO 8.1 8.2 8.2.1 I. II.	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES INTRODUCTION RESULTS Microhardness Indentation Microhardness of the Pure Cobalt and Co-SiC 8.2.1.1.1 Influence of microstructure 8.2.1.1.2 A model of microhardness for nano-composite Co-SiC coatings Co-Al ₂ O ₃ A. Influence of microstructure 8.2.1.1.3 A model of microhardness indentation for Co-Al ₂ O ₃ nanocomposite coatings	2 144 144 144 144 145 145 149 151 151
MECHAN NANOCO 8.1 8.2 8.2.1 I. II. 8.2.2	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES INTRODUCTION RESULTS Microhardness Indentation Microhardness of the Pure Cobalt and Co-SiC 8.2.1.1.1 Influence of microstructure 8.2.1.1.2 A model of microhardness for nano-composite Co-SiC coatings Co-Al ₂ O ₃ A. Influence of microstructure 8.2.1.1.3 A model of microhardness indentation for Co-Al ₂ O ₃ nanocomposite coatings Nanoindentation Test Micro indentation nanoindentation comparison	144
MECHAN NANOCO 8.1 8.2 8.2.1 I. II. 8.2.2 I. II.	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES INTRODUCTION RESULTS Microhardness Indentation Microhardness of the Pure Cobalt and Co-SiC 8.2.1.1.1 Influence of microstructure 8.2.1.2 A model of microhardness for nano-composite Co-SiC coatings. Co-Al ₂ O ₃ A. Influence of microstructure 8.2.1.1.3 A model of microhardness indentation for Co-Al ₂ O ₃ nanocomposite coatings. Nanoindentation Test Micro indentation-nanoindentation comparison Indentation size effect	144
MECHAN NANOCO 8.1 8.2 8.2.1 I. II. 8.2.2 I. II. 8.3	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES. INTRODUCTION	144 144 144 144 144 144 144 144 144 145 145 145 145 145 145 145 145 145 151 151 154 157 158 159 162
MECHAN NANOCO 8.1 8.2 8.2.1 I. II. 8.2.2 I. II. 8.3 8.4	ICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT MPOSITES. INTRODUCTION	144 144 144 144 144 144 144 144 144 145 145 145 145 145 145 145 145 145 151 151 154 157 158 159 162 164

CHAPTER 9:EFFECT OF HARDNESS AND ELASTIC MODULUS ON WEARRESISTANCE165

9.1 INT	IRODUCTION 1	65
9.2 Res	SULTS OF NANOINDENTATION	.65
9.3 Res	SULTS OF WEAR TEST 1	.67
9.4 Dis	SCUSSION	.76
9.5 Col	NCLUSIONS	.76
CHAPTER 1	0: DISCUSSION1	.77
10.1 PAI	RTICLES INCLUSION MECHANISMS	.77
10.2 ME	ECHANICAL PROPERTIES 1	.77
CHAPTER 1	1: CONCLUSION AND FUTURE WORK 1	.80
11.1 Co	NCLUSION	.80
11.1.1 1	PRP and an anionic surfactant technique for cobalt systems of Co-SiC and Co-Al ₂ O ₃ 1	80
11.1.2 1	Mechanical behaviour of the electroplated cobalt nanocomposites	81
11.2 FUT	TURE WORK 1	.82
REFERENCES	5	83
APPENDICES .	1	198

CHAPTER 1: INTRODUCTION

1.1 Background

Modifying surface properties of engineering materials to improve surface performance and service life has been considered as an important research topic for many years. It can be done by the treatment of the surface and near surface sections in order to achieve desirable properties that are distinct from the properties required from the bulk of the material. These properties include hardness, wear resistance and corrosion resistance that are required in functional applications of materials. Coating technology is one approach available for this purpose.

The most widely used high hardness, wear resistant and corrosion-resistant metallic coating is electroplated Engineering Hard Chromium (EHC). This has been used to improve surface properties for decades in numerous decorative and functional applications. These applications include: gage tools, machine parts, oil drilling rods, cylinders of internal combustion engines and aerospace applications, particularly landing gears and turbine engine components. However, the highly toxic hexavalent chromium salts have been restricted by the Permissible Exposure Limit (PEL) for Cr⁶⁺. All compounds that contain Cr⁶⁺ have been reduced under the legislation of Europe Registration, Evaluation, Authorisation and Restriction of Chemicals (EUREACH) and US Department of Labours' Occupational Safety and Health Administration (OSHA) for safety and environmentally reasons. In addition, the electrolytic efficiency of the EHC plating process is low compared with other electroplated metals and alloys, especially nickel [1] The brittleness of EHC coatings can also lead to micro or macro- cracked deposited layers [2]. These important factors are driving efforts to find suitable alternatives, with much recent research conducted to find alternative technologies to hard chrome. The most important technologies are as follows [3]:

- 1) Thermal sprays
- 2) Electroless nickel
- 3) Electrodeposited nanocrystalline coatings
- 4) Plated nickel-cobalt alloys

High Velocity Oxygen-Fuel (HVOF) thermally sprayed coatings have been used as an alternative to hard chromium for low volume, high- added- value-Line Of Sight (LOS), but it is not suitable for internal and complex shaped coatings [4]. Generally, it is believed that electroplating of nickel- cobalt and nanocrystalline and is the most effective hard chrome alternative technique [5]. The majority of the electroplating processes have conventionally used

nickel alloys in electroless or electrolytic coatings [5]. However, according to the environmental protection agency, nickel is considered to be the fourteenth most toxic and pollutant metal [5]. Therefore, nickel can only be used as a temporary solution and finding other alternatives is still required.

Recently, nanocrystalline electrodepositions have been introduced as environmentally acceptable alternatives with preferred coating properties. Many nanocrystalline electrodeposited coatings have been used such as pure metals (e.g. Ni, Co, Pd and Cu), binary alloys (e.g. Ni-P, Ni-Fe, Zn-Ni, Pd-Fe, and Co-W) or ternary alloys (e.g. Ni-Fe-Cr). Multi-layered structures or compositionally modulated alloys and metal matrix composites (e.g., Ni-with SiC in microscale particle size) [6] also have been used. Nickel and cobalt nanocrystalline electrodeposited coatings are used in most electrodeposition technique. Nickel-based electroplated coatings can be alloys such as Ni-W, Ni-W-B or composites for example Ni-Al₂O₃ [7]. Cobalt-based electroplated coatings can also be used either as alloys such as Co-P [8] nanophase alloys and Co-W [9].

Electrodeposition of metal matrix composites is a technique of particle codeposition during metal matrix electrodeposition. It can be considered as a desired method for coating production over the other coating techniques due to many reasons : (i) homogeneity of deposition even for complex shapes; (ii) waste encountered in other techniques especially dipping or spraying is reduced in electrodeposition, (iii) reduction of contamination, (iv) functionally graded materials can be produced using electrodeposition and the ability to process parts continuously, and (v) overcome multiple difficulties related to high pressure and high temperature as it is done at low temperature for aqueous solution[10]. Moreover, it is considered as a promising technique in terms of its low cost and simplicity [11, 12]. However, it is not appropriate to produce 'free standing' coatings with higher thickness (more than 200µm) [13].

Electrodeposited nanocomposites are promising materials due to their unique physical and electrochemical properties compared with pure metals [14]. However, nanocomposite electrodeposition can be considered as a challenging process due to the low wettability and difficulty of controlling the uniformity of the co-deposited particles suspension and dispersion. Several techniques have been used in co-electrodeposition coatings, including direct current (DC), pulse plating (PP), and pulse reverse plating (PRP) due to their versatile effect on the produced coating microstructure and properties. It has been reported that a pulse reverse current technique can be used to control and improve the reinforcement co-deposition, with enhanced

electrodeposited composites properties as a result [15]. Moreover, the composition of the deposited layers and the coating thickness can be controlled by optimizing the pulse parameters in pulse plating technique. This can promote grain nucleation, increase the grain density and hence produce grain refined deposits with higher strength than those produced by conventional electroplating techniques using direct current [15]. Hence, PRP can be considered as an effective technique to improve the hardness and wear resistance and to decrease the macro residual stress of the coatings compared to direct and pulse current methods. A new mechanism suggested by [16] included the use of anionic surfactants with PRP which can effectively aid the particles inclusion and produce well dispersed particles in the metal matrix. This mechanism has great potential for developing a generic technique for nanocomposite coating deposition.

The influence on the microstructure is considered an essential factor in understanding the mechanical behaviour of such nanocrystalline and nanocomposites materials. In this work, the electrodeposition of Co matrix films with different nanoparticles will be systematically investigated. The microstructural contribution (intrinsic effect) of the grain boundary and the particles dispersion effect in strengthening will be explored in order to give a better understanding of the evolving hardening. The extrinsic effect due to the length scale of the material test will also be considered. Finally the predicted and examined wear resistance of the Co-SiC nanocomposites will be investigated to give a full picture of the production of these nanocomposites.

1.2 Aims and objectives

The motivation for this project is divided into two categories and are summarised as follows:

1. Firstly, produce successful electrodeposited metal matrix nanocomposites (MMNC) of cobalt with a successful dispersion of nanoparticles. The nanoparticles will be in an electroplating bath. They will experience electrophoretic migration to the working electrode, where they should then be adsorbed and encapsulated by the growing metallic coating in such a quantity and with sufficient dispersion so as to confer desirable properties. The aim is to develop an optimised generic coating process to deposit Metal Matrix Nanocomposite Coatings (MMNCs). Also, suggesting possible ways to provide an experimental set up that allows new MMNCs to be developed with different combinations of matrix and nanoparticle to give innovative materials development which will be of great interest outside the scope of the project. The

successful electroplated nanocomposites with good dispersion goal can be achieved by the microstructural and mechanical assessments of those nanocomposites in order to optimise the parameters of selected coating systems for specific tribological applications, demonstrating functions such as wear resistance and lubricity.

2. The second main aim is to demonstrate the ability to control the coating properties by investigating microstructural contribution of the grain boundary strengthening and nanoparticle dispersion strengthening.

1.3 Thesis structure

This thesis is divided into the following chapters:

- **Chapter One**: Presents an overview of the study. It consists of a brief introduction, a statement of the aim of this work, and the structure of the thesis.
- **Chapter Two**: Comprises the theoretical background of the electrodeposition of the nanocomposites with a review of the relevant literature on pulse reverse plating of cobalt and nickel.
- Chapter Three: Provides a theoretical background of the length scale plasticity of polycrystalline structures to determine the microstructural contribution to hardening and the contribution of the extrinsic size effect, present in this study as an Indentation Size Effect (ISE).
- Chapter Four: Present the experimental work conducted for the attempts to produce Co-PTFE with high particle inclusion, nickel matrix with nano SiC nanocomposites as well as the production of pure cobalt metal /nanocomposites starting with the bath chemistry, the design of the electroplating bath, the electroplating parameters and the electroplating set up. A full description of the microstructural characterisation methodology is then covered. Finally, a detailed summary of the mechanical characterisation methods utilised in this project are presented.
- Chapter Five: Compares the microstructural characterisation results for pure cobalt coatings and Co-SiC nanocomposite coatings. The coating characterisation includes cross section analysis via field emission gun scanning electron microscopy, chemical composition analysis by EDX and XRD, and nano particle dispersion and grain size characterization of the cobalt matrix via TEM. The second part of this chapter covers the results for coatings produced with different particle loadings in the bath. Finally, the results are discussed in the context of the PRP and anionic surfactant mechanisms.

- Chapter Six: Presents the results for Co-Al₂O₃ nanocomposites produced for the first time, with an emphasis on the applicability of the mechanism through four different sections: 1) Coatings produced by direct current (DC) and different anionic surfactant.
 2) Coatings produced by PRP and the duty cycle effect. 3) Coatings produced by PRP and with an anionic surfactant SDS, which highlights the effect of the SDS concentration in the bath on the resulted incorporated nanoparticles. (4) Discussion of the results in terms of the deposited mass per cycle and the achieved cathode efficiency.
- Chapter Seven: presents the production of Co-PTFE composite coatings in an attempt to give understanding of the behaviour of such composite to be co-deposited with alumina in cobalt matrix in future work.
- Chapter Eight: The mechanical property assessments of the nanocrystalline Co/Conanocomposites for Co-SiC and Co-Al₂O₃ by indentation test (microhardness and nanoindentation measurements). A suggested strengthening model for the nanocomposites produced by PRP and specific surfactant content is presented in the context of the microstructural hardening theory derived in chapter three. Also, the ISE is considered as an external contributing hardening effect. The results are discussed and finally concluded with a brief chapter summary.
- Chapter Nine: This chapter demonstrates one of the key findings of the mechanical characterisation results taken from nanoindentation tests presented in chapter seven. This considers the elastic modulus measurements from this test to predict the wear resistance of selection of Co-SiC coatings of varied SiC volume fraction (1%-8.7% volume) and compares them to the comparable pure cobalt coatings. The second section presents the validation of the predicted wear resistance by pin on disc wear tests for the same selected coatings. A brief discussion of the results from both sections is presented with a short conclusion.
- **Chapter Ten**: This is the final chapter that gives a conclusion of the work done in this thesis and presents future work.

CHAPTER 2: LITERATURE REVIEW OF ELECTROPLATING OF NANOCOMPOSITES BY DIRECT CURRENT (DC) PULSE REVERSE PLATING (PRP)

2.1 Introduction

Electrodeposition of metals is a well-known technique for the formation of coating a layer of a metal on the surface of another. The process include the transfer of one or more electrons through the electrode/solution interface, **Figure 2.1**, shows a schematic diagram of the simple electrochemical cell resulting in the formation of a metallic phase. In this chapter, a brief description of the importance of the co-electrodeposition of the nanocomposites will be presented firstly with the emphasis on the electrochemical approaches employed to produce the nanocomposite coatings. Then, the mechanisms and models previously used for co-electrodeposition of composite coatings will be briefly described, namely those of electrochemical deposition and electrophoretic deposition. The affecting parameters on the co-deposition of the micro and nano composites will be considered. Particular emphasis is given to the effects of changes to the current for the co-electrodeposition. The results discussed in the literature are also reviewed with specific attention to the electroplating of pure cobalt, nickel, and composites with micro- and nanoparticles.



Figure 2-1:Schematic diagram of the basic electrochemical cell

2.2 Electrodeposition of nanocomposites

The start point of metal matrix composites electroplating can be traced back many year ago. In 1928 copper with graphite particles composite coating produced for an automotive bearing. The importance of the composite coatings has increased significantly in the following years of 1960s and 1970s due to the demand for coatings with high wear resistance and high hardness [17-20]. Many literature in that time concentrated on the use of hard ceramic particles like carbides, nitrides, and borides, composed in metal matrix with good mechanical properties such as Co and Ni as a replacement for the hard chrome. An example, is the electrodeposition of Ni-SiC composites coating for rotor tips of wankel engines, particularly by BMW then later by Porsche [19].

After that periods a number of composites coatings of nickel with wide range of particles in the form of spheres (i.e., SiC, Al₂O₃), tubes, polyhedrons and indeed various other shapes and types in order to produce composites with fascinating and extraordinary properties for corrosion and wear protection in the aerospace and automotive sectors [21-25].

Unfortunately, dispersion of nanoparticles in metal matrix is challenging as nanometre-sized particles tend to agglomerate due to their high surface energy. Also, it is difficult to keep the particles well suspended in the solution of the bath. This difficulty affects the rate of particle

dispersion in the metal matrix; as a result the properties of the nanocomposites will be influenced. Hence, good dispersion of the nano particles during electroplating is required.

According to the literature the particle incorporation into the metal matrix involves a number of common processes that includes: electrophoresis process that involves the particles migrating through the solution to the growing metal deposit under the influence of an electric field (positively charged ions migrate towards the negative electrode while the negatively charged ions migrate toward a positive electrode). The second process is the mechanical entrapment, where the particle encapsulation is independent of electrolyte composition and particle properties, adsorption and convective- diffusion [17-20].

The steps of the particles inclusion is explained in five steps: (1) formation of ionic clouds around the particle; (2) particle transport by convection to the hydrodynamic boundary layer; (3) particle transport by diffusion to the cathode; (4) the adsorbed free ions and electro-ions on the particles' surfaces are adsorbed at the cathode; and (5) electroreduction of adsorbed ions associated with particles' inclusion into the growing metal matrix. **Figure. 2.2** shows these steps.

Many parameters should be considered in order to achieve a successful co-deposited coating. These parameters include: particles characteristic (concentration, surface charge, type, shape and size) electrolyte composition, current type (DC, PRP), and agitation type and degree. The mechanism of the particle incorporation is still unclear and need more consideration. Understanding the mechanism of the particle incorporation is helpful to describe the particle co-deposition behaviour in the form of mathematical models. Such models should be able to suggest the content of the particle in the composite from a given process parameters. This will be helpful in screening the composite the composite and achieving optimization of the process condition for industrial applications.



Figure 2-2: The model for the deposition of Cu-Al₂O₃ coatings described by (Walsh et al, 2014)[19].

Figure 2.3 presents a representative diagram taken from a review paper by Walsh and Leon [19]. The diagram shows the general factors should be considered as input variables to predict a model that controls the particles inclusion, mechanical and physical properties, and the morphology of the coatings.



Figure 2-3: Diagram showing the input variables that should be considered to model the co-deposition of nanoparticle into metal matrix and the output results that can be obtained, the diagram is taken from a review paper by Walsh and Leon, 2014 [19]

2.2.1 Models

Mathematical models are essential in rationalising, simulating and predicting the relationships among the plating parameters mentioned above. Various theoretical models have been proposed to describe the inclusion of particles to produce co-deposited nanocomposites with the opposing controls of the physical dispersion of the particles in the electrolyte and the electrophoretic migration of the particle [19, 20]. However, these models need to be more flexible and reliable to explain the behaviour of a wide range of composite electrodeposited coatings. This was reported to be partly the result of the tedious and time-consuming work required to acquire a set of experimental data sufficient to validate a proposed model and the numerous interrelated process parameters involved [18]. It should be pointed out that the majority of the theoretical mechanisms developed to describe particle incorporation into a metal matrix have been developed for micron-sized particles. In this work the modelling of the co-electrodeposition of the nanocomposites will not be carried out. The models will be presented in order to give a better understanding of the achieved work so far to fill the gap in this topic as described in the following order:

Guglielmi [26] described the codeposition of micro particles in two successive adsorption steps: (1) particle approach the cathode surface and loosely adsorbed, and (2) Strong adsorption of the particle when they lose their ionic cloud.

In the first step, the particles are weakly adsorbed at the surface once they approach the cathode, and they are in equilibrium with the particles in suspension. The first step is of a physical nature, where the particles that are surrounded by a thin layer of the electrolyte ions move towards the cathode surface then weakly adsorbed. The surrounding layer formed around the particles will inhibit any direct contact and interaction with the cathode surface. Hence, the particles will remain weakly adsorbed till the second step.

The second step includes strong particle adsorption by Coulomb interactions and incorporation into the growing metal matrix deposit. The volume fraction of the incorporated particles, α , is given in equation 2.1 given below:

$$\frac{\alpha}{1-\alpha} = \frac{zF\rho_m V_o}{M_m i_o} \cdot e^{(B-A)\eta} \cdot \frac{kc_b}{kc_b+1}$$
(2.1)

Where:

 M_m : atomic weight of deposited metal; ρ_m : deposited metal density; i_o : exchange current density; z: valence of the electrodeposited metal; F: Faraday constant; η : electrode overpotential; c_b : bulk concentration of particles; k: Langmuir adsorption constant; A, B, and V_o : constants.

This model was used successfully to deposit a number of particles of SiC, TiO_2 , and Al_2O_3 . However, this model neglects the effects of hydrodynamic forces and particle characteristics [17, 18] that made some deficiencies of model for interpreting the co-depositing mechanisms.

Celis [27] recognized that Guglielmi's model could not interpret the peak particle content that can be achieved against the current density curve for $Cu-Al_2O_3$ codeposition. Celis suggested that deposition rate of the particles depends on the Cu^{2+} ions reduction rate that adsorbed on the particles. The study concluded that two processes are playing a vital role in the particles co-deposition mechanism:

- 1. The ions adsorption into the particle, and
- 2. Then, the reduction of the ions at the cathode electrode surface.

Celis suggested a model to calculate the weight percent of the co-deposited particles. The model hypothesis is that there should be a certain amount of adsorbed ions on the particle that reduced at the cathode surface in order to ease the particle incorporation [28]. Like former models this model could not predict the particles content directly from the experimental conditions, where some parameters should be determined by fitting the model with the experimental results.

Hwang and Hwang,1993 [29] suggested a more general model than Guglielmi and Celis, where various current density range was used to codeposited α -SiC into Co matrix. Based on Guglielmi model, the particle co-deposition rate is determined by the electrode reactions for adsorbed species on the particles, whose rates are determined by kinetic and/or diffusion parameters [29]. The model considers Co²⁺ and H⁺ adsorbed on the particles. Three varied range of current density are distinguished for the reduction of the adsorbed ions:

- 1. Low current density were only H^+ ions are reduced.
- Intermediate current density, where the H⁺ reduction rate has achieved its limiting value and also Co²⁺ is reduced.
- 3. High current density where for both ions the reduction rate is at its limiting value.

The model suggested that the rate deposition of the particle at low current density range is found by the reduction of the adsorbed H^+ ions [29]. While the intermediate current density range the particle deposition rate due to H^+ reduction is at its limiting value, and the metal deposition is i the same as for H^+ in the low current density range. Lastly, in the high current density range the particle deposition rate is only determined by diffusion and is independent of the current density and the adsorbed ions concentration. This model can be considered as an improvement of Guglielmi's model. Though, inherently the hypothesis is made that adsorbed ions reduction totally differs from that of free ions. The deposited metal efficiency competitive between the reduction of free H^+ and Co^{2+} , is deliberated to be independent of current density. While for adsorbed ions varied regimes are distinguished. A summary of the proposed models in codeposition of particle into metal matrix is given in **Table 2.1**.

The models mentioned above investigate particle inclusion with direct current (DC). Considerable research has been conducted that implements the suggested previous mechanisms, and which shows the inapplicability of those models in general as they typically

CHAPTER TWO: LITERATURE REVIEW OF CO-ELECTRODEPOSITION

only work for a particular bath and composite. Also, these models do not consider the interaction between the particles and the metal matrix and do not account for the quality of the particle dispersion [19].

Model	Characteristics and assumptions	Deposits and process conditions			
		Reaction	Particles size, µm	Current density, mA/cm ²	Rotation speed, rpm
Guglielmi, 1972 [26]	Describes both adsorption and electrophoresis. The particles are covered by adsorbed metal ions. Particle characteristics and electrolyte conditions are accounted for semi-empirically. The effect of flow is not considered.	Ni/TiO2 Ni/SiC	1–2	20–100	NG
Celis,1987 [30]	Uses probability concept to describe the number of particles that can be incorporated at a given current density. Mass transport of particles is proportional to the mass transport of ions to the working electrode. Volume ratio of particles in the metal deposit will increase under charge transfer control and decrease under mass transport control.	Cu/Al ₂ O ₃ Au/Al ₂ O ₃	0.05	0–90	400–600
Frasaer,19 92 [27]	Uses trajectory to describe the co- deposition of non-Brownian particles. Involves two steps: (1) reduction of metal ions (described by Butler-Volmer expression); (2) co-deposition of particle (described by trajectory expression).	Cu/PS Ni/SiC	11 0.01–10	0–80 0–200	0–700 0–2000
Hwang,19 93 [29]	An improvement of Guglielmi's model. Uses three modes of current density (low, intermediate, high) to distinguish the reduction of adsorbed ions on particles. Involves three steps: (1) forced convective of particles to surface; (2) loose adsorption on the surface; (3) irreversible incorporation of particles by reduction of adsorbed ions	Co/SiC	3	1–60	400
Vereecken , 2002 [31]	The transport of particles to the surface is controlled by convective-diffusion. The influence of particle gravitational force and hydrodynamics is accounted for at various current densities. Valid only when the particle size is smaller than the diffusion layer thickness.	Ni/Al ₂ O ₃	0.3	5–40	500–2000

 Table 2-1: Examples of the theoretical models used for the electrodeposition of composites containing particles [15]

2.3 Effective Parameters affecting the co-deposition of nanocomposites

In order to produce nanocomposites with improved particle incorporation and good mechanical properties (requiring good adhesion of the coating to the substrate and no voids), all the processing parameters should be optimised as discussed above. The expected influence of these parameters will now be briefly covered to provide some theoretical direction to the search for the optimum conditions to produce the nanocomposite with a brief review on the work that has done considering these parameters.

2.3.1 Effect of bath composition

Metal ion concentration, additives, complexes, and surfactants play a vital role in affecting the codeposition of particle into the metal matrix when the same types of particles are used. Different particles inclusion rate can be achieved from different baths types and using the same particle type. For example, previous work by Brandes and Goldthorpe [32] observed that Al_2O_3 particles codeposited into copper and nickel baths while not co-deposited in to chromate bath. The metal salt may also influence the particle incorporation rate into metal matrix. A study reported that $Cu-Al_2O_3$ composites was not deposited effectively from sulphate bath while successfully produced from copper cyanide bath. Increasing the primary metal salt concentration results in enhancing particle inclusion. This observation is supported by previous work on Cu and Ni baths [18, 33], and was reported to be due to the modified particle surface composition, which is determined by the adsorption of electrolyte ions. This is related to the impact of the negative zeta potential of the particles, which increases with increasing metal ion concentration in this case. The effect of the zeta potential will be given in more details in the next section.

2.3.2 Effect of particle characteristics

Particle type, shape, and their crystal structure are essential parameters in particle incorporation. Particles can be either conductive or non-conductive (inert). Both have their pros and cons for encapsulation into a metal. Molybdenum disulphide, chromium carbide, zirconium diboride are conductive particles. Conductive particles are characterized by their attraction to the metal matrix resulting in dendritic growth [34] and might be accompanied by increasing the coating roughness due to their selective deposition acting as a deposition site. Non-conductive particles promote a smooth surface on the deposited coatings. Hence, selecting
the particles depends on the required characteristics of the resultant films. Also, it was found that the absolute value of the particle content change for different systems. Likewise a study conducted by Greco and Baldauf [35] on Ni-TiO₂ [35] and Ni-Al₂O₃. The study found that the three times as much TiO₂ built in a nickel matrix as Al₂O₃ for the same plating conditions. Particle size and concentration should also be considered. Increasing particle loading in the bath increases the deposited particles' volume fraction as shown in previous works. For example, a study conducted by Hwang and Hwang [29] on cobalt composites using micron size of SiC found that increasing the particle content from 2 -10 g l⁻¹ increased the particle content in the cobalt up to 8.7 wt.% at constant other plating parameters. Increasing the particle loading in the bath beyond a certain content found to decrease the particle content in the coatings and proved in a number of studies. For example, a study on Bronze-graphite composites by Afshar et al [36] used different graphite particle loading 10-60 g l⁻¹. They found the particle content in the matrix reached a constant value up to ~ 8 - 9 vol. % at 50 g l^{-1} graphite loading in the bath. This is known as the saturation point, where a decline in the number of particles embedded in the matrix can be seen beyond that point and beyond this loading a noticeable decrease in the vol % of the particle content in the coatings. This was supported by other studies [20, 37]. Small particles incorporated more readily in term of numbers than large ones as reported in literature.

2.3.3 Electrolyte parameters

I. Surfactant effect

The role of the surfactant is important in promoting particle co-deposition. The surfactant presence promote the stability of a suspension by improving the wettability and the surface charge of the suspended particles. The modified surface charge prevents the particle agglomeration. Also, the surfactant improves the electrostatic adsorption of the particles suspended on a substrate [38, 39]. In order to give a better understanding of the surfactant effect it's important to define some relative terms:

Surfactant: are compounds that lower the surface tension between a liquid and a solid.
 Surfactants may serve as detergents, wetting agents, foaming agents, and dispersants.
 A surfactant molecule has two ends, a hydrophilic and hydrophobic. If surfactants are added to a suspended particle solution bath, the surfactant molecules may be adsorbed onto the particle surfaces with their hydrophobic ends next to the surface and the hydrophilic ends outward towards the solution.

- The surface energy of the particles: is the difference in the electrical potential of the inner and outer surface of the particles dispersed in a colloid which could be caused by ion adsorption. The surface charge results in electric field emission by the particles that attracts or repels the particles in the colloid and affects its properties.
- Zeta potential: is the electrical potential that available at the interface between a solid surface and its liquid medium, and a function of the particle's surface charge, any adsorbed layer at the interface and the nature and composition of the surrounding medium that particle suspended in. The particle's zeta potential magnitude is considered as a measure of this particle interaction. This means Zeta potential can be used to predict the suspension long-term stability. If the suspended particle have a large negative or positive zeta potential then they will tend to repel each other and resist aggregates formation. On the other hand, if the Zeta potential values of the particle was low, i.e. close to zero, then there will be nothing to inhibit the particles approaching each other and aggregating [40]. The common dividing line between stable and unstable suspensions is at either +30 mV or -30 mV, where particles with Zeta potentials more positive than +30 mV or more negative than -30 mV are generally considered stable [40, 41].

The adsorption of the surfactant on the particle surface results in developing the surface charge on the particle surface and prevents the particle agglomeration. Therefore, the stability of the particle suspended in the bath will increase. In addition, the promoted surface charge will increase the affinity of the particle to the cathode in baths that contain cationic surfactant. Hence, this will result in an increase of the particle inclusion to the cathode in DC plating. A previous study by a Japanese team established that cationic surfactant addition with the hydrophobic tail length of a surfactant containing an azobenzene group like 4- ethylazobenzene 4-oxyethyl trimethyammonium bromide(AZTAB) enhance the inclusion of the SiC particle into Ni matrix [42, 43]. The developed positive surface charge increases the affinity of these particles toward cathode and enhances the incorporation of particles in the coating accordingly.

For the anionic surfactant, the negative surface charge of the particle promoted by the surfactant made the particle repel each other, de-agglomerate them and keep them sustained in the electrolyte bath in similar way to the cationic surfactant as explained above. It's claimed that the cohesive forces between cations in the electrolyte and the particles could increase. Therefore, by moving cations toward cathode in DC plating and reduced at the cathode accompanied by particles capture in the growing coatings [44].

Surfactant type should also be considered in the co-deposition of the particle into metal matrix as research suggested that different surfactant that belong to the same group are also affect the particles incorporation into the metal matrix. Shrestha et al [42, 43] noted that the length of the Alkyl group bonded to the AZTAB moiety of the surfactant affect the AZATB efficiency to disperse the maximum amount of SiC particles into a nickel matrix. They applied the plating process of Ni-SiC nanocomposites in the presence of AZTAB surfactant having different lengths of alkyl groups (C0-AZATAB, AZTAB, and C4-AZTAB). It was found that an increase in the concentration of the AZTAB resulted in an increase of the particle codeposition up to a certain optimum AZTAB concentration. Beyond that concentration a decrease in the trend of particle codeposition was recognized.

The increase in the particle trend co-deposition was attributed to the strong adsorption of AZTAB on particles, which might increase the positive charge on the particles, and hence, increases the affinities of these particles for the cathode. Thus, the maximum amount of co-deposited SiC particles was found to be 71.5, 62.4, and 50.4 vol. % by using these surfactants. These difference on the extent of particle codeposition arise due to the difference in the rate of adsorption of AZTAB surfactants from the particle surface in the vicinity of the cathode.

The pH of the bath also influences the surface charge of the particle and their incorporation into the metal matrix as a result. Likewise, the particle charge measurements of SiC powder in aqueous solution showed that in the pH range of 5-11, zeta potential of the powder is highly negative. Therefore, the cationic surfactant is electrostatically adsorbed on the SiC particles developing a positive charge on the particle surface. Hence, an addition of the cationic surfactant prevents the particle agglomeration and improves the particles stability. Under the effect of the electric field, the developed positive surface charge of the particles showed high affinity toward the cathode enhancing the particle incorporation into the matrix.

In addition, surfactants are used to suppress hydrogen evolution. For example, one particular anionic surfactant (saccharin) is used to overcome hydrogen evolution. However, the disadvantage of the free unadsorbed surfactant molecules is in the brittleness of the resultant deposit as surfactants might adsorb onto the coating surface [18]. The brittleness could be attributed to the inclusion of O in the metal matrix. Weston et al. [16] studied the incorporation of WS₂ into Co matrix and using CTAB. The resulted coating experienced a noticeable brittleness that attributed to the oxygen adsorption into the Co matrix, which was confirmed by

EDX analysis, as the reduction reaction was hindered by the adsorbed CTAB molecules on the working electrode with their hydrophobic tails facing the solution.

II. Effect of temperature

The codeposition of the composite performes at temperature of typical to the bath temperature. Some previous works reported an important effect of the temperature on the particle inclusion [17, 45]. It was claimed that the thermal energy activates the movement of the particles towards the working the electrode up to a limited temperature. A study carried out by (SL Kuo, 2004) [46] on Ni-Mo₂ composites and at different temperature 30- 50 ° C. The study showed an increase in particle content from 18-22 vol. % with increasing the electrolyte temperature 30 - 50 ° C. Above that temperature the particle incorporation into the deposit decrease due to the effect of the thermodynamic movement of the ions no seen effect of temperature on the particle inclusion. Some other research showed no seen effect of temperature on the particle encapsulation as reported in literature [47, 48].

In this work, the temperature will not be considered, as the temperature will be fixed during all the experiments duration.

III. Effect of bath agitation

One major problem with nanocomposite electrodeposition is the particle mono dispersion in the electrolyte bath due to the surface energy, which makes the particles agglomerate in high conductivity metal electrolytes. This results in non-uniform particle encapsulation, and hence an efficient agitation method is required. Bath agitation helps to both achieve and maintain proper suspension of the particles in the electrolyte and delivery of particles to the cathode by virtue of their movement. Increasing the level of agitation results in an increment in particle volume fraction in the deposited coating. On the other hand, research has shown that an excessive agitation results in lower particle concentration through the deposit [17]. This lower particles to be removed from the cathode surface before being entrapped. Generally, two types of techniques have been using to keep the particles in suspension. These are: (1) physical dispersion of the particles by agitation, and (2) surfactants addition [49]. Physical dispersion by magnetic stirring has been mostly used for laboratory investigation. It prevents the settling of particles within the electrolyte bath. Further agitation, by using an ultrasonic system that will be considered in this work has been investigated in a number of research. This effect will

be discussed in details in the following sub-section. Other methods for agitation are out of the scope of this work and can be found in a number of papers [17, 19, 20].

Ultrasound implementation in composite co-electrodeposition process has been found to be beneficial to enhance the particles dispersion and de-agglomeration in the electroplating bath. Also, it can improve a fine dispersed particle with a uniform dispersion through the metal matrix [50].

Applying ultrasound to a liquid bath results in acoustic cavitation phenomena. If the ultrasound power is high enough, a cavity or bubble can be formed in the liquid bath. When this bubble or cavity grows to a critical size it reaches a point, with high temperature and pressure, where it can become unstable and collapses violently, **Figure 2.4**.



Figure 2-4: Bubble growth and implosion in a liquid irradiated with ultrasound [50]

The temperature and pressure at which this happens depends on the applied power and frequency. At this point, liquid jet streams form that break down the agglomerated particles and keep them suspended in the electrolyte and prevent their agglomeration due to the vibration effect. The nano particle can be jetted on to the surface due to the effect of the micro jetting phenomenon resulted by the bubble collapse. Hence, improved particles inclusion can be achieved and their dispersion and as a result improves the mechanical properties of the coatings, as reported in previous literature [50, 51].

A recent study conducted by (Tudela et al., 2015) [52] using the ultrasound and stirring during the co- electrodeposition of a nanocomposite will be discussed in details due to its importance in the current study. (Tudela et al., 2015) produced Nickel- hexagonal boron nitride (Ni-hBN)

and WS₂ particles with no surfactant and by DC supported by ultrasound and overhead stirring agitations. The effect of the agitations on the particle dispersion were investigated separately and combined in three different conditions: overhead stirring of 300rpm, ultrasound of 0.18 W cm⁻³, and combined effect. The agitations effect on the particle dispersion in the bath and through the coatings cross section. The results found that the best particle dispersion in the bath achieved by the combined agitations types used in the study, followed by the ultrasound agitation only. The results were discussed as follow:

- 1) The mechanical agitation contributed to achieve a more homogeneous dispersion, preventing the larger agglomerated particles from sinking to the bottom of the beaker.
- The ultrasound enhanced the de-agglomeration of agglomerated particles due to the formation of cavitation bubbles and the physical effect inherently related to their presence.

The cross section of the coatings from Ni-WS₂ and Ni- hBN plated under mechanical agitation showed large agglomerates hBN particles with a less homogeneous distribution, while finer particles were noticeably seen in the electrodeposited composite coatings under the ultrasonic and combined agitations conditions. Yet, coatings plated under ultrasound only offered higher particles content than the ones plated under combined ultrasound / mechanical agitations. The results of the cross section from both nanocomposites were attributed to the setup of the ultrasound in the bath and how can that interact with the stirring of the electrolyte. The particle inclusion into the coatings were affected by the mechanical agitation that claimed to be counteract the ultrasound effect. A parallel flow to the cathode surface caused by the mechanical agitation by the overhead stirring. The overhead stirring proposed to be the reason behind some particle removing from the near surface of the substrate. This was resulted in a reduction in the particle concentration at the cathode-substrate interface and decreasing the particle content in the coating. No quantitative data were given in the mentioned study for the change in the particle inclusion with changing the agitation method.

Increased particle incorporation from coatings produced by the combined methods was explained according to the effect of the mentioned mechanical agitation. As the cavitation bubbles close to the surface would also be affected by the overhead stirring action and be less effective in the area close to the cathode surface. This would decrease the particles ability to de-agglomerate accordingly. The findings of this study could be considered when using agitation combined with the ultrasound agitation and consider the flow direction caused by stirring, which will be the magnetic stirrer in this project. Another study by (García-Lecina et al, 2012) investigated the co-deposition of Al_2O_3 nanoparticles into nickel matrix. Two different agitation were applied, mechanical agitation using the magnetic stirrer and the ultrasound agitation. The results confirms the findings from the previous mentioned study were a higher nanoparticle content was achieved by the ultrasound compared to the magnetic stirrer. The particle content incorporated into nickel matrix using the ultrasound reached 2.2 wt. % and 1.8 wt. % using the magnetic stirrer at 25 g l^{-1} particle loading.

Some other studies applied the ultrasonic irradiation before the electrodeposition process [50, 53]. This could be combined with surfactant addition for further improvement of particle dispersion [50]. The effect has been investigated in a number of previous studies. (Cojocaru et al, 2005) examined the effect of pre-treatment the electroplating bath of the nano composite Au-nano diamond by ultrasound. It demonstrated that Au- diamond bath subjected previously to the ultrasound produces coatings with higher particle content that reached 0.55 wt. %, even if the ultrasound was not used during the electrodeposition process itself [54].while the coatings produced from bath that did not subjected to the ultrasound contained 0.4 wt.% of diamond nanoparticles. The study found that the cavitation's field and oscillating acoustic pressure led to micro-turbulence, acoustic steaming and micro - jetting. Micro- jetting results in high-speed particle collisions and breaking of the van der Waals forces. It should be mentioned that the ultrasound parameters, including the power, frequency and the ultrasound equipment are important. These parameters should be considered during the electroplating with the use of ultrasound. However, it is out of the scope of this study as the power parameter kept constant throughout all the experiments as will be described in experimental chapter.

IV. Effect of current density

Current density is a main parameter controlling the concentration of particles involved in the metal matrix. The effect of current density varies with bath compositions [20]. Low current density lowers the number of adsorbed ions and complexes in a double layer onto the cathode. Increasing the current density will result in increasing the number of adsorbed ions, making the process controlled by activation [17]. Commonly, the highest particle content range exists within the normal limits for the optimum current density range for the electrodeposited metal matrix and this suggested to be the guidance for the choice of current density for composite plating but this behaviour could be complex as shown in previous studies. A study conducted by (Walsh et al, 2015) [55] on Ni –SiC system with different current density. The particle inclusion in nickel matrix reached 50 vol. % at current density range 4 - 6 A dm⁻². At higher

current densities, the silicon carbide content in the nickel matrix coatings steadily reduced to 10 vol. % at 100 mA cm⁻². These findings were supported by other studies on nickel [24] [56].

2.3.4 Electrodeposition control techniques

Electrodeposition techniques are fundamentally divided into potentiostat and galvanostatic. For co-electrodeposition techniques, the galvanostatic techniques have been essentially used [17]. Three different techniques used for co-electrodeposition of metal matrix nanocomposite coatings are direct current (DC), pulse current (PC) and reverse pulse current (PRC).

I. Co-deposition by direct current (DC):

Direct current has commonly been used to produce electrodeposited nanocomposites. This depends on the concept of nanoparticles inclusion to metallic matrix that occurs concurrently with the reduction of an ionic species to form the metal surface. A number of studies investigated the particles incorporation into metal matrix using direct current. For example: Podlaha and Landolt (1997) studied the effect of direct current on the produced nanocomposite Cu-y Al₂O₃ with particles size of 30 nm. They found that co- electrodeposition of Al₂O₃ to Cu by DC produced low concentration of particles that reached 1.68 wt. %. Another study (Weston et al) [16] looked at DC co-electrodeposition of inorganic fullerene (IF-WS₂) nano-particles with cobalt matrix without and with considering the surfactant effect. Three bath were used: no surfactant, SDS anionic surfactant and CTAB cationic surfactant. There results of the bath with no surfactant proved unsuccessful particle co-deposition as the particles agglomerated forming a thick scum on the surface of the bath and very few particles were observed in the Co matrix formed by DC plating, which was less than 1 wt. %. This indicated the difficulty of codeposition of WS₂ nano particles in metallic matrix. Coatings produced with CTAB showed smooth surface with concentrate dispersed IF-WS₂ particle and accompanied by high oxygen content that reached 9.7 at. % towards the outer surface and 13.6 at. % near the substrate region. The high particle content is attributed to the adsorption of CTAB surfactant to particle surface resulted in developing the positive surface charge of the particle and increasing the affinity of these particle toward cathode in DC plating as explained previously in the cationic surfactant effect. The behaviour was modelled as shown in Figure 2.5-i. The high content of oxygen was resulted by the adsorbed CTAB molecules on the working electrode with their hydrophobic tails facing the solution and produced cracked and brittle coatings. This confirmed the effect of the cationic surfactant explained previously.

CHAPTER TWO: LITERATURE REVIEW OF CO-ELECTRODEPOSITION

The last bath in Weston et al study was cobalt bath with WS_2 and SDS surfactant. The results showed very low particle content and that was discussed as that the SDS confer the WS_2 nanoparticle a negative charge and repel them resulting in low particle inclusion during the deposition. This behaviour was also modelled as explained in **Figure 2.5-ii**.

(i) CTAB cationic surfactant and DC plating



(ii) SDS Anionic surfactant and DC plating



Figure 2-5: Model of the nanoparticle WS₂ behaviour into Co matrix taken from a previous study [16] : (i) from cobalt bath with CTAB surfactant, (ii) from cobalt bath with SDS surfactant

II. Co-deposition by Pulse Reverse Plating (PRP):

Pulse electrodeposition PED is a plating technique where a standard, stationary DC current is changed with its modulated forms, Figure 2.6 shows both waveforms. The pulse plating allowed to control the composition of the film and its thickness by regulating the amplitude and width of the pulse [15, 57, 58]. They favour the grain nuclei initiation and reported that they enhance the grain number per unit area producing a finer deposited grain with improved properties compared to the conventional plating method by DC [15]. According to the literature, PRP used occasionally in the early of the 1940s and 1950s to plate the cyanide copper [57]. There are different types of pulsed forms which have been studied. The applied current waveform can be divided into two categories: (1) unipolar, where all the pulses are in one direction and (2) bipolar, where both of the anodic and cathodic pulses are mixed. Typical waveforms contain: (1) cathodic pulse followed by a period with zero current in the anodic pulse, (2) direct current (DC) with superimposed modulations, (3) duplex pulse, (4) pulse-onpulse, (5) cathodic pulses followed by anodic pulses-pulse reverse current (PRC), (6) superimposing periodic reverse on high frequency pulse, (7) modified sine-wave pulses and (8) square-wave pulses. The square wave pulses have the advantage of an extensive duty cycle range [59] and will be considered in this project. The square waves are considered as the simplest waveforms to produce, however, the sequences of pulses can be programmed to attain quite complex waveforms [57].

In pulse current deposition, the following parameters can be controlled:

 I_c : refers to anodic current; I_a : refers to cathodic current; t_c : is the cathodic cycle time; and t_a : is the anodic cycle time. Duty cycle: this represents the real time during the cycle that deposition is effective and is given by the following equation:

Where

$$D = \frac{(Q_c - Q_A)}{Q_c} \tag{2.2}$$

 Q_C and Q_A are the cathodic and anodic charge per cycle in the PRP technique and can be calculated using the following formula:

$$\boldsymbol{Q}_i = \boldsymbol{I}_i * \boldsymbol{A}_s * \boldsymbol{t}_i * \boldsymbol{N}_{cycles} \tag{2.3}$$

CHAPTER TWO: LITERATURE REVIEW OF CO-ELECTRODEPOSITION

Where A_S is the surface area of the specimen, I_i is the current, t_i : time, and N_{cycles} is the number of cycles.



Figure 2-6: Typical waveform under i) DC and ii) Pulse reverse current

During reverse-pulse current deposition, the total metal plated during the t_c should exceed the metal dissolved during the anodic time t_a for overall plating to arise. In an extreme case, when the charge reduced exactly equals the charge dissolved, no metal is plated. This fixes the minimum value of peak current, which can be applied during reverse-pulse current plating for a given reverse current density [60]. Also, it's advocated that as the peak current is raised or the t_c lengthened, larger and more stable crystallites are formed, which lead to more compact deposits [60]. On the other hand, raising the reverse current results in the complete dissolution of small crystallites and only larger crystals continue to grow [60].

The pulsed electrodeposition technique has been implemented in numerous studies to improve the dispersions of particles because some of the metal matrix is dissolved during the reverse pulse resulting in higher particle incorporation compared to the DC plated coatings [19]. The pulsed electrodeposition technique has been implemented in many studies in an attempt to improve the dispersions of particles and to understand the mechanism of their incorporation. These studies concentrated on using alumina particles in either Cu or Ni metal matrix. Former studies [7, 61, 62] by (Podlha et al) for the copper γ -alumina system, suggested that employing long steady-state pulses reverse current with long pulse time allows for three main advantages for the co-deposition of composites compared to DC plating. These advantages are: (1) enhancing the number of particles through the deposit; (2) allows for a decrease in the required particle concentration in the electrolyte; (3) selectively entrapping nanoparticles of a similar size; and (4) providing the possibility of partial dissolution of large particles from the deposit. The study claimed the particle content enhancement that was 4.7 wt. % compared to 1.68 wt. % in the coating to be attributed to the electrolyte type used. Wang and Wang [63] studied the co-deposition of Ni nano carbon fibre with 100-200 nm in diameter and 10-20 µm in length by PRP and DC. A cationic polymer agent was used to disperse the carbon fibre. The plating's parameters of the PRP are given in Table 2.2. The carbon fibre content within the nanocomposites was determined by electron probe X-ray micro analyser (EPMA). The analysis demonstrated that PRP produced higher nano fibre content that reached ~ 5-6 wt. %, while the content was about 2-3 wt. % in DC. Additionally, the number of pulse cycles on the particle inclusion was investigated. The results showed that at low number of pulse cycle (1) several isolated carbon nanofibers was achieved, (2) the number of carbon nanofiber increased when increasing number of cycle to 4. At 40 cycles, the number of nanofiber increased. The codeposition mechanism of the nano carbon fibre was explained as follows: prior to the electrodeposition, the metal ions and carbon nanofibers were flown adjustment to the cathode electrode. Applying the current to the substrate resulted in immediate fine grain reduction of the metal ions in close contact to the cathode surface. The carbon fibre available in the bath incorporated subsequently into the film of the growing metal. The nano carbon fibre is suggested to be able to serve as pair of cathode due to their high conductivity. This process would be repeated simultaneously with the dissolution of the nickel in the anodic cycle. The study claimed that as the duration of the cycle increases, a larger amount of the carbon nanofibers will co-deposited with nickel progressively to make nanocomposite Ni-carbon nanofiber. This work demonstrates that PRP can be used successfully to increase the particle inclusion in the metal matrix, but it requires a high particle loading in the bath to be able to compete the high metal deposition rate.

Table 2-2: Plating parameters of Ni with nano carbon fibre from a previous study [64]

ic (A.dm ⁻¹)	ia (A.dm ⁻¹)	$t_{c}(s)$	t _a (s)	t _{off} (s)
4.5	9	30	5	30

A recent study by Weston et al. [16] attempted to make a Co-WS₂ nanocomposite coating by PRP for use in tribological applications. Weston used inorganic fullerene IF-WS₂ (130 nm

diameter) particles in a CoSO₄-gluconate bath and ultrasonic agitation. In order to achieve success, it is essential to achieve dispersion of the nanoparticles into the electroplating medium. Anionic and cationic surfactants were employed to attain well dispersion in the bath. The surfactant was used to promote particle dispersion (by promoting wetting of the solid surface of the particles) whilst ensuring at the same time that they do not incorporate into the electrodeposited layers or participate in the chemical reaction. Weston found that the controlled particles' rate of inclusion is affected by the type of surfactant, type of current (PRC) and DC, and the duty cycle (cathodic cycle, and cathodic time t_c). A well-dispersed set of particles with 11 vol. % in a Co matrix coating layer was produced using PRP and an anionic surfactant. Consequently, a new mechanism for the electrodeposition of IF-WS₂ in a Co matrix by PRC and anionic surfactant was suggested. The mechanism includes the adsorption of the anionic surfactant onto the nanoparticles, conferring a negative charge. Electrophoresis brings the particles to the near working electrode region during the anodic phase of the PRC cycle, Figure 2.7-1 followed by adsorption of the particles onto the working electrode and then encapsulation during the cathodic phase of the cycle, Figure. 2.7-2. This followed by the deposition of another cobalt layer followed by the particles encapsulation Figure 2.7-3 and 4. Crucially, this allowed control over the particle content of the coating from the same bath. This mechanism has the potential for developing a generic technique for the deposition of nanocomposite coatings.



Figure 2-7: Model for behaviour of particles during PRP plating in the cobalt bath with SDS
 (1) Electrophorese effect in the anodic pulse (2) particle encapsulation during the anodic pulse,
 (3) switching to the cathodic pulse and repulsive effect on particle and attracting Co²⁺ (4) metal depositing during the cathodic pulse [16]

In this work, this suggested mechanisms will be investigated further microstructurally and mechanically considering the input parameters and output results suggested in a previous review paper [19] to investigate its applicability for the different systems of Co nanocomposites and Ni matrix nanocomposites. The following section will give a brief literature about the work done for the co-electrodeposition of these composites.

2.4 Co-matrix nanocomposite electrodeposition

The other desired type of coatings for tribological applications is the electrodeposited cobalt that possess high hardness and wear resistance either as alloys or nanocomposites [29, 65-67]. Cobalt matrix nanocomposites can offer comparable or better mechanical properties compared to nickel matrix nanocomposites, particularly for high temperature applications [68]. The electroplated cobalt can be electroplated with different hardness and wear resistance properties depending on the alloying elements and the incorporated particles. Reviewing the work that has done on cobalt will be helpful to set up the bath composition and plating conditions. Only a few previous studies have considered the co-electrodeposition of cobalt composites [16, 29, 69] with particle size 1-3 µm. Hwang and Hwang ,1993 [29] investigated the effect of current density in DC plating in the range 0 - 6 A dm⁻² and the stirring speeds. The results showed low and high current density and corresponding to 0.5 and 4 A dm⁻² can achieve high particle inclusion that reached ~ 9, 5.3, 4, and 2.8 wt. % at 4 A dm⁻² current density and particle loading of 10, 5, 4, 2 g l⁻¹ respectively. This was combined with the lower stirring speed. It should be noted that the microstructural characterization of the coatings and the mechanical characterization was not considered in this study. Another study was proposed by (Rudnik.et al) [69] for the Co- α SiC system with SiC particles size of 4µm and with different bath compositions using DC. Two different current densities were used, and different loadings of 10-50 g l⁻¹ SiC were added to the bath to investigate the behaviour of the system, which is considerably high particle content. The results of the particle content analysis were measured by image analysis and showed high particle incorporation from 15-36 vol. %. (Rudnik.et al) suggested that higher current densities can achieve this high particle content. Also, the study reported that increasing the particle loading of the bath to 50 g l⁻¹ enhanced the particle content with no apparent saturation point. Further investigation of the coatings hardness in the same study revealed that the microhardness of the produced coatings were of values range 200-280 HV~ 215- 250 HK for these coatings for the high particle contents 15-36 % but no pure cobalt

coatings produced in the mentioned study to compare the results. The achieved hardness in the mentioned study is much lower than the hardness of the hard chromium reported in literature that is in the range of 600 - 1000 HV ~ 625-1055 HK [70]. Weston .et al [16] on Conanoparticles WS₂ with 130 nm used low anionic surfactant 0.2 g l⁻¹ SDS content for the cobalt system. The study used two different baths of two different cobalt concentration 0.05 M and 0.2 M and cationic and anionic surfactants to promote the particles inclusion. The work found that higher cobalt concentration a high particle content in the coating and brittle coatings. The study did not consider the mechanical properties of those produced coatings.

CHAPTER 3: LENGTH-SCALE PLASTICITY THEORY AND STRENGTHENING MECHANISMS OF NANOCOMPOSITES

3.1 Introduction

Understanding the influence of the microstructure on a materials response is essential to improve the design and reliability of a range of engineering applications. This effect depends on the materials constituents. For metals this depends on whether they are pure metals, alloys or part of a metal matrix composite. In this chapter, the improvement of a coating's mechanical properties by the construction of nanocomposites is investigated. The nanocomposite can be defined as a composition of two separate phases or more that have nanocrystalline or amorphous structure. In the literature it is well known that nanocomposites and nanostructured materials have different performance and display new unique properties compared to that of conventional materials. The reason for the improved strength of nanostructured materials is due to their small internal length scale. The internal, or intrinsic, length scale of a material is determined by the size of the dominant features in the microstructure. The relevant features and their associated length scales are discussed in the next section. Additional "extrinsic" length scales can also be influential. These are typically the size of the specimen, in this case the thickness of the coating, and the test length scale, which is the indentation depth for the type of indentation testing considered in this thesis. The contribution of these different length scales is considered here and developed into a consistent unified approach through the concept of a mean free path for dislocation movement.

3.2 Intrinsic Length Scales

The four dominant strengthening mechanisms in metals are considered here.

3.2.1 Precipitation hardening

It's the kind of strengthening caused by the interaction between dislocations with coherent or non-coherent particles depending on the description of the particles geometry and spatial distribution of particles. The nanocomposites produced in this work include the use of nano SiC and Al₂O₃ particles, where the nanoparticles are effectively impenetrable to dislocations at room temperature where the plastic deformation remains athermal.

If the dislocations considered as independent obstacles, which results by spacing them widely and with no strong elastic field overlap, the constrains can be modelled as point obstacles in the slip plane. When a dislocation is moving over its slip plane under the action of shear stress τ . It acts approximately as a flexible, extensible string with a constant line tension $\Gamma = \frac{\mu b^2}{2}$, where μ represents the solid shear modulus, and b is the magnitude of the Burgers vector of the dislocation. Once the moving dislocation meets an array of barriers that restrict its motion, it presses against them to create local configurations as shown before[71] and is presented in Figure 3.1. The dislocations bow out between surrounding obstacles with increasing the shear stress resulting in a circular arc with a radius that is proportional to the spacing between the precipitates [72]. When the stress increase up to a critical value the dislocation can be driven past the precipitates. This shear stress is known as the critical shear stress, τ_c . This is a function of the obstacle strength and the geometry of the obstacle distribution. These factors are represented in the model by the dimensionless constant β_P , where the subscript P denotes that it relates to precipitates [72]. The critical resolved shear stress for random and square arrays of obstacles has been calculated by Orowan [73] to be the shear stress required to expand a loop of dislocation between the particles

$$\tau_P = \beta_P \frac{\mu b}{L_P} \tag{3.1}$$

where L_P is the distance between precipitates. It is anticipated that $\beta_P = 0.5 - 0.8$ [72]. Typically, we expect $5 < \mu b < 20$ so length scales of a micron equate to stresses of the order of 10MPa or less. Consequently, length scales much above this are expected to make little significant contribution. For a regular array of precipitates, the distance between the particles is given by

CHAPTER THREE: LENGTH-SCALE PLASTICITY THEORY AND STRENGTHENING MECHANISMS OF NANOCOMPOSITES

$$L_P = 1.6r_P\left(\sqrt{\frac{\pi}{4f}} - 1\right)$$
(3.2)

where r_p is the mean precipitate radius and f is the precipitate volume fraction.



Figure 3-1: obstacles bowing in Orowan strengthening (Gladman, 1997)

The above model implies that a dispersion of small precipitates is more effective at strengthening a metal than a dispersion of large precipitates of the same volume fraction. It should also be noted that this is only true up to a point. If the precipitates become too small then it becomes energetically more favourable for a dislocation to cut through the particle than bow around it, as shown in **Figure 3.2**. The figure shows that at the maximum critical radius the highest strengthening can be achieved. This is typically about 5 - 30 nm. Below that radius the precipitates can be cut through by dislocations and the strengthening effect is weakened.



Figure 3-2: The critical radius for the precipitation hardening by the second phase particles [74] Solid solution strengthening

This is only relevant in alloys. This thesis is associated with a pure metal matrix, and hence this is largely included for completeness and is relevant to further work. Large solid solution atoms sit in the matrix and create an elastic field, which hinders the movement of dislocations. Their affect can be considered in a similar manner to precipitates, although the solid solution atoms are less effective barriers than precipitates. The critical shear stress is therefore similar to **Equation (3.2)**

$$\tau_S = \beta_S \frac{\mu b}{L_S} \tag{3.3}$$

where the relevant intrinsic length scale is the mean distance between solute atoms. Here we expect a lower value for the effective strength of these obstacles, such that $\beta_s = 0.01 - 0.05$ [72]. For an atomic concentration *c* of solid solution atoms the separation is predicted to be

$$L_S = \frac{b}{c^n} \tag{3.4}$$

where $n = \frac{1}{2}$ for dilute concentration and $n = \frac{2}{3}$ for higher concentrations due to strain field interactions [72].

3.2.2 Forest hardening

This is strengthening due to the "forest" of immobile dislocations which hinder the motion of other dislocations through it. Again, the dislocation obstacle field can be treated in a similar way to the two previous cases such that

$$\tau_F = \beta_F \frac{\mu b}{L_F} \tag{3.5}$$

where it is expected that $\beta_F = 0.1 - 0.3$ [72], making dislocations more effective strengtheners than solid solution atoms, but less effective than precipitates.

At this point it is useful to introduce the concept of the dislocation density

$$\rho = \frac{nl}{V} \tag{3.6}$$

where *n* is the number of dislocation lines, *l* is the average length of those dislocation lines, and *V* is the volume of the material they are in. The dislocation density therefore has units of $1/m^2$. It is possible to show that the average spacing between dislocations is

$$L_F = \frac{1}{\sqrt{\rho}} \tag{3.7}$$

such that (3.5) becomes the more widely used expression for forest hardening

$$\tau_F = \beta_F \mu b \sqrt{\rho} \tag{3.8}$$

The one difference between forest hardening and the previous two mechanisms is that the dislocation density can change during the deformation as dislocation sources are activated and their number increases. This leads to a decrease in the intrinsic length scale during deformation, which is typically observed as strain hardening. It will be shown later that for the self-similar indenters used for hardness testing in this thesis, the strain under the indenter is approximately constant. As a consequence, it is also reasonable to assume that the dislocation density, and the intrinsic length scale associated with forest hardening (3.7) is also constant. This will be the assumption for the remainder of this work.

3.2.3 Grain boundary strengthening

Grain boundaries are also obstacles to dislocation motion in a solid, but they are different to the three previous obstacle types in that they completely enclose the dislocations and can therefore not be by-passed by the bowing mechanism proposed by Orowan. To consider the effects of grain boundaries it is useful to introduce the concept of a mean free path, or slip distance, for dislocations to travel before they encounter an obstacle.

Slip distance theory assumes that the total accumulated plastic shear strain γ_p in a bulk sample is given by the Orowan equation

$$\gamma_p = b\rho_m \overline{x} \tag{3.9}$$

where ρ_m is taken to be the mobile dislocation density and \overline{x} is the mean free path of the dislocations. This inherently assumes that the mean free path does not change during the plastic deformation, and effectively just defines what we understand to be the mobile dislocation density, such that

$$\rho_m = \frac{\gamma_p}{b\overline{x}} \tag{3.10}$$

The total dislocation density defined by (3.6), $\rho = \rho_m + \rho_{im}$, consists of mobile (glissile) and immobile (sessile) dislocations. If it is assumed that the proportion of each is constant, so that it is possible to write $\rho_{im} = \lambda \rho_m$, where λ is a constant.

In a polycrystalline material (with no other obstacles), the mean free path will be half the average grain size (assuming dislocation sources are uniformly distributed through the grain) such that the relevant intrinsic length scale for grains is $L_G = \bar{x} = \frac{1}{2}d$.

Combining (3.10) and (3.8) gives the combined contribution from grain boundary strengthening and forest hardening

$$\tau_{GF} = \beta_F \mu b \sqrt{\lambda \left(\rho_0 + \frac{\gamma_p}{bL_G}\right)}$$
(3.11)

CHAPTER THREE: LENGTH-SCALE PLASTICITY THEORY AND STRENGTHENING MECHANISMS OF NANOCOMPOSITES

where ρ_0 is the initial dislocation density. If we assume the initial dislocation density is low such that $\frac{1}{\sqrt{\rho_0}} \ll d$, then we recover the familiar Hall-Petch relationship

$$\tau_Y = \tau_0 + \frac{k}{\sqrt{d}} \tag{3.12}$$

where τ_0 is introduced to represent the intrinsic strength of the crystal without obstacles.

At this point it is useful to note that the scaling with length is different for grain size, scaling as $\frac{1}{\sqrt{L_G}}$ as opposed to $\frac{1}{L_F}$ etc like the other mechanisms. This is because in the assumed mechanism, the grains strengthen the material by activating dislocation sources and increasing the number of dislocations within the grains, leading to hardening of the grains through forest hardening. As the deformation continues, all dislocations will become immobile as the pile-up against the grain boundaries, suggesting that $\lambda \to 1$ as the plastic shear strain increases.

This assumes that grain boundaries are impenetrable by dislocations, and that the applied shear stress is sufficient to easily activate dislocation sources within the grains. The source strength can be an important influence on the critical shear stress, but this is not typically the case in hardness testing, where the onset of plasticity is almost immediate, and surface and sub-surface sources are very active. Taking this into account, the contribution from the activation stress for sources is not considered further in this thesis.

3.3 Extrinsic Length Scales

It has been observed that the strength of materials increases as the extrinsic (test) length scale reduces [75]. As this thesis is concerned with the testing of thin coatings, where the indentation depth must be much less than the coating thickness in order for the effects of the containing materials (substrate and encapsulation) not to influence the measurements. Hence, the coating thickness is removed as a test length scale. The indentation depth can influence the result, however, in a phenomenon known as the Indentation Size Effect (ISE).

3.3.1 Strain gradient hardening

The ISE is commonly explained by strain gradient plasticity, whereby geometrically necessary dislocations (GNDs) must be present in the material to accommodate the plastic deformation of the material. The GND density is related to the plastic strain gradient through the Burgers vector. For example, for a beam with longitudinal axis x and through thickness axis y the GND density is largely determined by a single dominant plastic strain gradient

$$\rho_{GND} = \frac{1}{b} \left| \frac{d\epsilon_x^p}{dy} \right| \tag{3.13}$$

The contribution from forest hardening (3.11) can now be written as

$$\tau_{GF} = \beta'_F \mu b \sqrt{\rho_0 + \rho_{GND} + \frac{\gamma_p}{bL_G}}$$
(3.14)

where we have written $\beta'_F = \beta_F \sqrt{\lambda}$. The dislocations contributing to the non-GND population, $\rho_0 + \frac{\gamma_p}{bL_G}$ are not related to the test-length scale, but only the intrinsic material length scale. These are referred to as statistically stored dislocations (SSDs).

3.4 Combining Length Scale Effects

The simplest model for combining the different strengthening mechanisms is to add them together such that

$$\tau_Y = \tau_0 + \tau_P + \tau_S + \tau_{GF} \tag{3.15}$$

or

$$\tau_{Y} = \tau_{0} + \mu b \left(\frac{\beta_{P}}{L_{p}} + \frac{\beta_{S}}{L_{S}} + \beta'_{F} \sqrt{\rho_{0} + \rho_{GND} + \frac{\gamma_{p}}{bL_{eff}}} \right)$$
(3.16)

CHAPTER THREE: LENGTH-SCALE PLASTICITY THEORY AND STRENGTHENING MECHANISMS OF NANOCOMPOSITES

3.4.1 Indentation Testing

The hardness of a material is related to its yield strength, as proposed by (3.15) above. Here we assume the Nix-Gao model for GND formation as it is the simplest. Geometrically necessary dislocations (GNDs) are injected from the surface by the action of the indenter to achieve the required plastic deformation. The indentation model of Nix-Gao [76, 77] is derived here for a conical indenter shape. This is valid for all self-similar indenters, i.e. not spherical indenters such as Vickers, Berkovich, and Knoop etc. The first assumption is the relation between the critical shear stress τ_Y and the hardness

$$H \approx 3\sqrt{3}\tau_{Y} \tag{3.17}$$

During indentation, GNDs are injected downwards from the surface. This creates surface steps the height of the Burgers vector b on the surface. This is illustrated for a conical indenter in **Figure 3.3**.



Figure 3-3: Assumed geometry of GNDs below the indenter.

The indenter has been retracted showing the permanently indented surface. The left-hand side shows the continuum version, the right-hand side the discrete (stepped) surface profile with the injected GNDs beneath. Assuming purely plastic deformation, these steps must match the depth

CHAPTER THREE: LENGTH-SCALE PLASTICITY THEORY AND STRENGTHENING MECHANISMS OF NANOCOMPOSITES

profile of the indent. The plastic zone is assumed to be a hemi-spherical region below the indenter. The radius is the contact radius of the indenter, a. This is defined by $\delta(a) = 0$. A GND at radius r is therefore considered to be a circular line of length $2\pi r$ which has descended a distance y below the surface. Given the spherical shape of the plastic zone, this is given by $r^2 + y^2 = a^2$. The spacing between the GNDs is defined by the slope of the indenter profile such that

$$\frac{1}{s(r)} = -\frac{1}{b}\frac{d\delta}{dr}$$
(3.18)

At radius r the dislocation density (due to a single GND) is given by

$$\rho_{GND}(r) = \frac{l}{V} = \frac{1}{s(r)y(r)}$$
(3.19)

where $l = 2\pi r$ is the dislocation line length and $V = 2\pi r s y$ is the cylindrical volume containing each dislocation loop (of thickness *s* and depth *y*) within which it has moved. The average dislocation density is therefore

$$\overline{\rho}_{GND} = \frac{1}{\overline{sy}} \tag{3.20}$$

where the average vertical mean free path of the GNDs is given by

$$\overline{y} = \frac{1}{\pi a^2} \int_0^a 2\pi r y dr = \frac{2}{a^2} \int_0^a y^2 dy = \frac{2a}{3}$$
(3.21)

where the definition of y above means that rdr = -ydy which has been used to make the integral easier. It now only remains to define the indenter profile $\delta(r)$ to calculate s from (3.18) and hence ρ_G from (3.20) and therefore H from (3.17).

For a conical indenter, the indentation profile is defined by $\delta(r) = h\left(1 - \frac{r}{a}\right)$, where $tan\theta = \frac{h}{a}$. From (3.18) we get

$$\frac{1}{s} = \frac{h}{ba} = \frac{tan\theta}{b}$$
(3.22)

CHAPTER THREE: LENGTH-SCALE PLASTICITY THEORY AND STRENGTHENING MECHANISMS OF NANOCOMPOSITES

which gives a constant spacing between GNDs (as the indenter slope is constant), so, $\bar{s} = s$. Then (3.20) is easily determined to give

$$\overline{\rho}_G = \frac{3tan\theta}{2ab} \tag{3.23}$$

Combined with the Orowan equation (3.9) this also tells us that the average plastic shear strain in the hemispherical zone under the indenter is

$$\gamma_P = b\overline{\rho}_{GND}\overline{x} = b.\frac{3tan\theta}{2ab}.\frac{2a}{3} = tan\theta$$
(3.24)

And so the final result (3.8) is

$$\tau_{Y} = \tau_{0} + \mu b \left(\frac{\beta_{P}}{L_{p}} + \frac{\beta_{S}}{L_{S}} + \beta'_{F} \sqrt{\rho_{0} + \frac{3 \tan^{2} \theta}{2bh} + \frac{tan\theta}{bL_{eff}}} \right)$$
(3.25)

or

$$H = H_1 + \Delta H_{\sqrt{1 + \frac{h^*}{h} + \frac{L^*}{L_{eff}}}}$$
(3.26)

where $H_1 = 3\sqrt{3}\left(\tau_0 + \mu b \left(\frac{\beta_P}{L_p} + \frac{\beta_S}{L_S}\right)\right)$ is principally due to precipitation hardening and solid solution strengthening, $\Delta H = 3\sqrt{3}\beta'_F\sqrt{\rho_0}$ is the forest hardening contribution before work hardening due to additional dislocation nucleation, $h^* = \frac{3\tan^2\theta}{2b\rho_0}$ is the length scale associated with the onset of the extrinsic length scale and $L^* = \frac{2h^*}{3\tan\theta}$ is the length scale associated with the onset of the intrinsic (material) length scale to forest hardening. This shows that the hardness increases as the indentation depth *h* decreases giving the expected indentation size effect.

Equation (3.26) will be used to interpret the contributions of the various strengthening mechanisms in the nanostructured composite coatings.

CHAPTER THREE: LENGTH-SCALE PLASTICITY THEORY AND STRENGTHENING MECHANISMS OF NANOCOMPOSITES

In this thesis, the grain boundary length scale dominates the effective length. For macrohardness measurements, the ISE can be neglected as $h \gg h^*$. Also, solid solution strengthening is not an issue in a pure metal matrix so $L_s \rightarrow \infty$. Hence it is proposed that (3.26) can be approximated by

$$H = H_0 + \frac{A}{L_p} + \frac{B}{\sqrt{\mathbf{d}}}$$
(3.27)

Where: A: is $\mu b \beta_P$, B: $\mu b \beta_G$, for the analysis of the microhardness tests.

CHAPTER 4: METHODOLOGY AND EXPERIMENTAL WORK: NANOCOMPOSITES COATING PREPARATION AND MICROSTRUCTURAL CHARACTERIZATION TECHNIQUES

4.1 Introduction

This chapter presents the experimental work regarding attempts to produce nanocomposites from cobalt metal matrix. The effect of particle characteristics (concentration, size, type) on the dispersion of nanoparticles through the matrix will be investigated. The production includes the materials used and the electrodeposition procedure. Microstructural characterisation was performed to study the coating morphologies and microstructures. The texture of the coatings was also investigated, and crystallite size measurement undertaken via XRD and TEM. Crystallite size measurements were estimated from XRD by considering the instrumental peak broadening effect. Then, hardness tests were performed in micro and nanoindentation to study hardening of the Co and Co-SiC and Co-Al₂O₃ produced by PRP and SDS anionic surfactant. Nanoindentation tests were performed for comparison with microhardness tests to study the ISE. Additionally, indentation tests were used to predict the tribological performance of the cobalt and the nanocomposites. Finally, Co-SiC coatings with nano SiC 0-8 vol. % were tested in a comparative wear test of sliding wear resistance. A flow chart diagram is shown in **Figure 4.1** that clarify the parameters that was considered and the steps followed in this work.



Figure 4-1: Schematic chart explaining the experimental work implemented in this research considering the plating parameters in similar way according to the literature [19].

4.2 Coating Production

Three different composites were produced: nano Co-SiC with one selected surfactant content, and Co-Al₂O₃, and Co-PTFE with different surfactant content. In order to study the effect of SiC nanoparticles on the metal matrix, samples were prepared with and without nanoparticles. The bath chemistry was otherwise unchanged.

4.2.1 Materials

I. Pure Co and Co-SiC system with controlled particle loading and different particle sizes

The chemicals used in this chapter were obtained from various suppliers as detailed in **Table 4.1**. All chemicals were used as received without further purification. The chemical composition of the cobalt bath is the same as in the previous work [16]. Hydrated cobalt sulphate $CoSO_4.7H_2O$ was used as a source of Co^{2+} ions, boric acid (H₃BO₃) was used as a

buffer. Sodium chloride (NaCl) to increase conductivity, and sodium gluconate was used as a complexing agent. An anionic surfactant (SDS) with a 0.2 g l^{-1} content was used to form a suspension of the nanoparticles through cobalt. The basic bath chemistry for each of the coatings, with and without particles, is given in **Table 4.2**. The bath was operated at 80° C and at pH 6 which was attained by titrating concentrated NaOH solution into the aqueous solution of the salts with copious stirring.

Firstly, pure cobalt electroplated coatings were produced with the same chemical composition in the bath to act as a basis by which to compare the microstructural and mechanical properties subsequently produced. This coating was denoted B1, as can be seen in **Table. 4.3**. Coatings were produced by pulse reverse plating (PRP) with the following conditions: $I_{anodic} = 0.32$ A, $t_{anodic} = 10$ s, $I_{cathodic} = 0.16$ A, whilst $t_{cathodic}$ was variable 30, 40, 60, 90, and 120 s as will be explained in details in the following section. The number of cycles changed so that total $t_{cathodic}$ = 3600 s. Hence, the total Co deposition time remained constant, but the number of cycles varied with the length of the cathodic cycle.

Nanocomposite coatings were prepared for Co-SiC from baths containing one selected SDS content and different particle content. This work expands on the preliminary work [78] mentioned in chapter two with SDS content of 0.2 g l⁻¹, which resulted in particle content of approximately 13.4 vol% at tc= 30 s, **Figure 4.2**. Different particle loadings (10, 15, and 20) for further understanding the effect of particle loading a selected t_c = 60 s was chosen to plate with 25 g l⁻¹. Particle size for the mentioned different loading is (50 nm) as provided by the supplier, **Table 4.3**. The same electroplating conditions was used for B1 so that the effect of these variables on the number of nanoparticles co-deposited into the cobalt matrix could be determined. Nanocomposite coatings were denoted as B2, a-d.



Figure 4-2: Co-SiC with 0.2 g l⁻¹ SDS vol. % against cathodic time, t_c produced from an earlier work by Weston[78]

Chemicals	Purity%	Suppliers
CoSO ₄ ·7H ₂ O	98	Alfa Aesar
H ₃ BO ₃	99	Alfa Aesar
NaCl	99.5	Fisher scientific
Na-Gluconate	97	Alfa Aesar
Sodium Dodecyl Sulphate (SDS)	99	Alfa Aesar
β-SiC (45-55) nm	98.5	Alfa Aesar
β-SiC (30) nm	95	Alfa Aesar
Al ₂ O ₃ (40-50) nm	99.5	Alfa Aesar
PTFE (1) µm	99 ⁺	Aldrich

 Table 4-1: Chemicals used with suppliers

CHAPTER FOUR: EXPERIMENTAL WORK AND METHODOLOGY

CoSO ₄ ·7H ₂ O	H ₃ BO ₃	NaCl	Na-Gluconate	Sodium Dodecyl
				Sulphate (SDS)
80 g l ⁻¹	40 g l ⁻¹	30 g l ⁻¹	110 g l ⁻¹	0.2 g 1 ⁻¹
0.25 M	0.6 M	0.25 M	0.55 M	

Table 4-2: (Co-SiC) Bath composition

Table 4-3 Nano (SiC) particle loading-size in Co-SiC

Loading (g l ⁻¹)	Particle size (nm)	Bath No.
0	-	B-1
5	50	B-2a
10	50	B-2b
15	50	B-2c
20	50	B-2d

All the chemicals were weighed and added to deionized water and then mixed in a glass flask. SiC nanoparticles were added to the cobalt plating bath and stirred with a magnetic stirrer for 24 hrs to achieve a good suspension of the particles throughout the chemical bath.

The working electrode, was made from mild steel shim coated with zinc substrate and had dimensions of 20 x 20 mm, the counter electrode was cobalt (99.9% Sigma Aldrich) with a 30 mm diameter, whilst the reference electrode was Ag/AgCl. Before the deposition, the working electrode was washed with concentrate nitric acid for 5 s to remove the Zn coating and etch the mild steel, then washed in 10% (w/v) hydrochloric acid. The sample was then transferred to the plating bath and deposition initiated within 30 s to avoid reoxidation. After each experiment the coated samples were rinsed with deionized water and acetone to dry them.

II. Co-Al₂O₃ and Co-PTFE systems

The PRP technique is possibly generic, allowing the co-deposition of any particle into a Co matrix. To test this hypothesis, Al₂O₃ and PTFE particles were sourced, and an attempt was made to co-electrodeposit them in cobalt using pulse reverse plating (PRP) and an anionic surfactant for the first time.

Al₂O₃ nanoparticles (50 nm, Alfa Aesar) were added to the standard cobalt bath. A series of experiments were performed using the same experimental parameters as those used to produce Co-W₂S [16].

PTFE (1 µm) particles were also added to a standard Co bath to co-deposit into the cobalt in an attempt to produce a coating with combined high lubricity and hardness for tribological applications. Both Al₂O₃ nanoparticles (40 - 50 nm) and PTFE (1 µm) particles were added to the prepared baths and agitated for 24 hr before electroplating. Electroplating experiments were performed using different cathodic time and different numbers of cycles so that total cathodic time was always 3600 s. To investigate the effect of anionic surfactants and PRP duty cycle on the microstructural characterization and mechanical properties of the coatings, five different concentrations of SDS ranging from 0.0 to 0.8 g l⁻¹ were subsequently added to the bath. Higher surfactant content (up to 1 g l⁻¹) was excluded as it could result in the coating becoming brittle, as demonstrated in previous studies [67, 78]. The resulting baths were denoted as baths 3a to 3e (for Co-Al₂O₃) and 4a to 4e (for Al-PTFE), as per **Table. 4.4**.

SDS concentration (g l ⁻¹)	Co-Al2O3 bath	Co-PTFE Bath
0.0	3a	4a
0.2	3b	4b
0.4	3c	4c
0.6	3d	4d
0.8	3e	4e

Table 4-4: Co-Al₂O₃ and Co-PTFE

4.2.2 Electrochemical design

The design and size of the electroplating bath affects the co-deposition of the particles into the metal matrix. It affects the flow rate caused by stirring and ultrasound agitation position used in this work indicated in the literature [19]. A previous study considered the distance between the sample and the ultrasonic source. They found that changing the distance between the sample and the ultrasound tip from 5 mm to 25 mm resulted in changing the coating morphology and roughness. Hence, to design an electrochemical cell with larger bath capacity compared to the previous work, the electrochemical cell setting and design showing in Figure.4.3 was considered to maintain the same exact bath setting. Also, to keep the distance between the ultrasound source to the sample, and counter electrode, distance between ultrasound tip to the back of the bath, distance between counter and working electrode, and size of the bath container as in the previous work of Weston [16]. This was performed by designing a cell plug that fit to the new bath size and achieve the same setting as in the previous work to avoid any variation in unstudied electroplating parameters, see **appendix I**. It should be emphasized that the ultrasound effect during the electroplating by PRP was not considered in previous reports in the literature. So this current work further demonstrates the ultrasound effect on the dispersion of nanoparticles through the chemical bath combined with the surfactant SDS effect in PRP and how this can affect the inclusion of particles in the coatings.



Figure 4-3: Electrochemical cell setting with 500 ml bath, and 52 mm spacing between the counter and the working electrodes that mentioned in details in appendix I

4.2.3 Electrochemical cell set up

The plating parameters were selected to achieve particle variation according to previous work [16]. The duty cycle, as defined in (2.2) and shown in **Figure 2.5**, represents the fraction of time during the deposition process that is effective for plating. The plating parameters of the electroplating for all of the experiments are shown in **Table. 4.5**. For both cobalt systems the anodic time (t_{anodic}) was fixed during all the experiments at 10 s and the cathodic time (t_c) was varied as 30, 60, 90, and 120 s with a cathodic pulse current of -4 A dm⁻² followed by an 8 A dm⁻² anodic pulse. For nickel coatings, the cathodic time and anodic time was fixed to 60 s and 10 s, respectively, as per **Table.4.5**. All the measurements were carried out with three electrodes connected to an Autolab-type potentiostat using the Nova 1.60 software to adjust the current and time. Stirring was provided by an electromagnetic stirrer at a rate of 100 rpm for the cobalt system. Further agitation was supplied by an ultrasonic (Masonic Sonicators S-4000-010) using a Ti horn at 20 W and 20 kHz of power and frequency respectively. This compound technique was used to avoid agglomeration and maintain the dispersion of the particles in the electrolyte. The temperature was set at 80°C during all experiments.

Similar plating parameters mentioned for Co-SiC, **Table. 4.5**, were used for the coelectrodeposition of alumina that was subsequently carried out with cathodic cycle periods of 30, 40, 60, 90 and 120 s, whereas for PTFE experiments cathodic cycle periods were limited to 30 and 60 s, and for bath 2a to 60 s, respectively.
CHAPTER FOUR: EXPERIMENTAL WORK AND METHODOLOGY

t _c (s)	t _a (s)	Duty cycle	$I_c(A dm^{-2})$	$I_a(A dm^{-2})$	
Co – SiC					
30	10	0.43	-4	8	
60	10	0.71	-4	8	
90	10	0.81	-4	8	
120	10	0.86	-4	8	
3600	-	1.00	-4	-	
	Co-Al ₂ O ₃				
30	10	0.43	-4	8	
40	10	0.57	-4	8	
60	10	0.71	-4	8	
90	10	0.81	-4	8	
120	10	0.86	-4	8	
3600	-	1.00	-4	8	
Co – PTFE					
30	10	0.43	-4	8	
60	10	0.71	-4	8	
3600	-	1.00	-4	-	

Table 4-5: Electroplating parameters

4.3 Microstructural Characterization with advanced electron microscopy and X-Ray Diffraction

4.3.1 Scanning electron microscopy (SEM)

Scanning electron microscopy is a kind of electron beam technology uses to characterize the crystal structure and defects, elemental identification, and surface morphology. The characterization is carried out using different signal including secondary electron (SE), back scattered electron (BSE), characteristic x-ray (energy dispersive spectroscopy, EDX). EDX analysis is using for the elemental analysis of a specimen. In this work, the particle content through the electroplated coatings was determined.

I. Sample preparation

For the morphology observation, all the specimens' topographies were observed directly. While for the microstructure and the compositional analysis all the specimens were cross sectioned, mounted in a Struers CitoPress-1 mounting press with an epoxy resin, and labelled in a preparation for grinding and polishing. Different silicon carbide papers were used for the grinding of the mounted specimens ranging over 180, 240, 400, 600, 800, and 1200 grit for 30 s for each paper. The specimens were subsequently polished with 6 and 3 μ m diamond. Finally, 0.04 μ m colloidal silica paste was used as a final polish for all the specimens. All the samples were washed when moving to the next grinding and polishing stage, and finally washed with water, acetone and dried for SEM characterization and microhardness indentation.

II. SEM characterization

Cross-sectional images and topography observation were assessed using the Field Emission Gun (FEGSEM), Jeol 7800F at Loughborough University. Secondary electrons (SE) and back-scattered electrons (BSE) modes were used for the observation. Energy dispersive X-Ray spectroscopy (EDX) analysis was performed using Philips XL30 environmental scanning electron microscopy at the University of Leicester and EDAS INCA suite version 5.05, with voltages of 20 kV and 5 kV. FEGSEM images and EDX results were acquired from five evenly distributed positions across each coating, while three different cross-sectioned positions were selected for thickness measurements. For the PTFE particle nanocomposite coatings, EDX analysis was expected to give inaccurate results due to the effect of the chemical composition of light elements, namely the C and F (C_2F_4). Hence, image analysis was additionally undertaken in this instance. For this purpose, the accelerating voltage was reduced to 10 kV for coatings containing PTFE particles to limit beam penetration. To avoid any error between image analysis and EDX results, additional FEGSEM and EDX data were obtained from the centre of the coatings from bath 5a and 2 under high magnification, **Figure 4.4**.



Figure 4-4: Procedure for close up analysis of bath B- 3a and 4-coatings, showing:
 Sample of a close-up image of one of the coatings. ii) The same sample from the same sample after applying threshold to obtain the volume fraction.

4.3.2 Transmission Electron Microscopy (TEM) Imaging

TEM can be used to provide information about the structure of the crystal, growth direction, point defects and chemical structure. In this work, TEM characterization was performed using a JEOL JEM-2100 LaB6 TEM to present a picture of the effect of the PRP on the particle dispersion through the cobalt matrix. TEM was also used to gain an approximate crystallite size for a particular part of the chosen sample as well as to study the agglomeration of the nanoparticles. The TEM sample was prepared using Focused Ion Beam (FIB) milling, as it is less time consuming and is site- specific. This offers the possibility of choosing a specific area of the coating for examination. FIB microscope is similar to the SEM as it can produce a high-resolution image directly from the specimen, but in this case a finely focus ion beam rather than an electron beam is using for the imaging. The FIB system consist of an ion column, a sample stage, a vacuum chamber, detector and a source of an ion usually liquid metal ion sources (LMIS) for example (In, Bi, Sn, and Ga) ion source[79, 80], (Ga) is the most used one because of its combination of low melting temperature (30 ° C), low volatility and low vapour pressure, as well as being typically more stable. Ga ion source consists of a spiral wound Ga reservoir and a tungsten needle.

The sample was prepared using an *in situ* welding lift-out technique, as described in a review on the FIB technique [80]. The basic details of this technique can be found in [81]. One of the advantages of using FIB is that it enables the return of the sample to the FIB instrument for additional thinning after being analysed using TEM. The TEM sample preparation using the FIB procedure can be explained as follows. Firstly, the specimen surface was imaged with electrons and secondary electrons to choose the extraction site for the sample. Then, the selected position, as shown in Figure. 4.5-i, was deposited with a protective platinum strap with typical dimensions 20 x 4 µm and 4 µm depth and a large stair FIB with a 5 and 3 nA current trench. Then it was milled on both sides of the area of interest to reach an approximate 1 mm thickness of the specimen, as per Figure. 4.5-ii, iii. Carbon strap can be also used for deposition. The specimen was tilted at about 7° with respect to the ion beam. Then, a J cut shape was made in preparation to releasing the specimen using 10 pA. Before releasing the sample, a carbon weld or platinum is used to attach the sample to a needle (tungsten needle) and the sample was lifted out and away from the substrate. The specimen was then thinned by tilting the stage 1.28° positive and negative with respect to the ion beam direction to achieve parallel sidewalls. Also, this would make the specimen electro transparent to approximately 100 nm, as reported in [82]. The specimen thinning was monitored using the SEM. Finally, the specimen was cleaned using a low voltage, and the bulk of the sample removed and the extracted specimen transferred to a TEM grid in preparation for TEM observation.



Figure 4-5: FIB milling of a specimen of a Co-SiC sample in sequence: (i) the selected area of the specimen;(ii) two rectangular trenches with the deposited Pt at the top of the specimen; (iii) extracting the specimen by welding it to the W needle; and (iv) attaching the sample to the Cu TEM grid in preparation for thinning

4.3.3 X-Ray Diffraction (XRD)

X-ray diffraction is a powerful technique that is used to characterize crystalline materials. In the contrast to (SEM, EDS, XPS, and TEM) methods that provided information about the

surface of coatings (thin sections of the surface), XRD analysis used to provide information for the bulk surface of the produced coatings. Many information can be obtained by using XRD which include: structure, texture of the crystalline, available phases, grain size and crystal defects. In this study XRD analysis performed to study the effect of particles inclusion on the resultant crystal structure and grain (crystallite size) of the nanocomposites electrodeposited coatings and their crystallographic orientation effect on the resultant crystallites size. The theory pf XRD and the calculation of crystallite sixe will be explained below.

I. Theory of XRD

X-rays are produced by an X-ray cathode tube that consists of two metals electrodes enclosed by a vacuum chamber. The X-rays are filtered and directed toward the tested sample. The incident x-ray beam penetrates the material surface and reflected in consecutive parallel planes. Superposition of the scattered rays occurs as all X-rays reflected at the same direction. If we assumed that two parallel wavelengths travelling through crystallographic planes and separated by w distance **Figure. 4.6**, the second wave travels a longer distance than the first wave by BC and CD. If Δ (BC+CD) is an integer multiple (n=1, 2, and 3) of the wavelength (λ):

$$\Delta = n\lambda \tag{4.1}$$

Then constructive interference will occur. Destructive interference occurs in other cases when $(n = \pm 1/2, \pm 3/2)$. Hence, maximum sharp intensity arises from the sample only at specific angle when equation (4.1) holds with no intensity in between. These angles are given by:

$$\Delta = 2T \sin \theta \tag{4.2}$$

20 is the angle between incident and reflected X-ray beams (diffraction angle). Combining the two Equations (4.1) and (4.2) gives the Bragg equation (4.3) [83] which explains the principle of XRD analysis in terms of the reflection of XRD by sets of planes lattice.

$$n\lambda = 2T\sin\theta \tag{4.3}$$



Figure 4-6: geometry used for the simplified derivation of Bragg equation

II. Crystallite size analysis in XRD

Crystallite or grain size of nanocrystalline materials calculation is realised either by direct analysis using TEM or using X-ray diffraction analysis (X-ray line broadening). As the TEM characterization is a time consuming technique, especially for the high number of the coatings produced in this study, the XRD technique was used to estimate the crystallite size of these coatings.

Principally, in XRD the diffracted line should be very narrow, however, polycrystalline materials crystallite size results in line broadening if it below 1000 Å. This arises because of incomplete destructive interference [84]. If the incident ray is slightly off the Bragg angle, the reflected beam that would invalidate it originates from N planes inside the crystal. For crystallites that have sizes smaller than 1000 Å, the majority of the planes do not have their destructive counterparts N planes away [84]. This leads to the appearance of finite diffraction lines which are seen at the setting of the off Bragg angle and line broadening. The smaller the crystallites the wider the peak width is, and this is called size broadening. This inverse proportionality was found for small powder particles [84]. This has enabled XRD technique for the calculation of size of the scattering crystallites.

In addition to the sample line broadening (β), the broadened peaks in XRD analysis might result from the distortion of the lattice of perfect atoms in a crystalline material (the effect of the strain field caused by crystalline lattice defects like stacking faults and dislocations) and due to the instrument and the measurement conditions [85]. Furthermore, the profile width and shape do not only depend on the crystallites mean size, it is also affected by the crystallites shapes and size distribution [86-88]. Therefore, these effects should be considered and the instrumental effect denoted as b must be convoluted from the total experimental broadening function (B) to find an accurate evaluation of the crystallite size. Many approaches are using to determine the shape of the peak of the specimen, which will be discussed in the next section. Then, the instrumental broadening contribution will be discussed in details.

Peak shape

Many mathematical functions describe the respective instrumental line shapes and sample broadening. The most frequently used functions are the Gaussian, Lorentzian, and the Cauchy functions. If the line shape (due to a combination of instrumental and sample broadening) is assumed to have a Gaussian line shape, then the broadening line effects are related as following [89]:

$$B^2 = b^2 + \beta^2 \tag{4.4}$$

For all profiles that assumed as a Cauchy function, the line breadth is convoluted as:

$$\boldsymbol{B} = \boldsymbol{b} + \boldsymbol{\beta} \tag{4.5}$$

If the shape of the sample broadening assumed as Cauchy function approximately and the instrumental broadening is approximately Gaussian, then the relation can be given as [90]:

$$\frac{\beta}{B} = \sqrt{1 - b^2/\beta^2} \tag{4.6}$$

In XRD, the shape of real Bragg profiles is the convolution of multiple functions and rarely described by one simple function. It's usually a mixture of Gaussian and Lorentzian distributions [91]. Convoluting these contributions requires a numerical integration or changing the peak shape function parameters. A number of studies [91-93] reported that a good function to describe the diffraction peaks is the Pseudo-Voigt function, which is a linear combination of the Gaussian and Lorentzian functions. This function is used instead of the convolution of the Gaussian and Lorentzian functions.

Instrumental calibration

In order to convolute the instrumental effect, profile fitting a calibration standard is required to find the instrumental profile of the used diffractometer. The calibration curve is produced

CHAPTER FOUR: EXPERIMENTAL WORK AND METHODOLOGY

using the same instrumental conditions exactly same as the used for the experiments condition and using a standard sample. A number of suggested procedures are using for the instrumental line broadening convolution. One of the simplified method was implemented and discussed in this study. The simplified procedure includes mixing the standard with the sample and by running the XRD experiment a diffracted line close to the sample diffracted line will be produced. Otherwise, an external standard analysed under the same conditions as the sample can be used [94]. Using this procedure with any kind of the mentioned standards, the pure diffraction pattern breadth can be estimated either by **Equation (4. 4)** or (4. 5). If the line shape assumed to have a Gaussian line shape, **Equation (4. 4)** is derived, while the (4. 5) equation for the line of Cauchy shape. A previous study [90] stated that the Cauchy profile may be used to estimate β at the existence of crystallite size distribution as it gives a good approximation.

Previous studies confirmed that the used standard should possess some characteristic requirements [95]. These characteristics are outlined below:

- a) Not contribute to the peak profile of the measured sample (electroplated Co-SiC and Co-Al₂O₃ coatings in this study).
- b) Few overlapping or preferably no, overlapping peaks with the sample.
- Macrocrystalline: large grained, crystallite size larger than 500 nm, and less than 10 μm particle size.
- d) Defect and strain free.
- e) Same absorption coefficient as the measured sample.

Also, it should be emphasised that the standard sample can be an external reference or an internal reference as reported [96]. A number of references material use for the calibration, some of the used references are: Silicon standard (Si NIST SRM 640c), lanthanum Hexaboride (LaB6 NIST SRM 660a) which is a convenient powder standard, and alumina powder (Corundum SRM 1976b). The available reference material for this study is the corundum SRM 1976b, which is using specifically as an instrument profile correction standard. And it used as an instrumental calibration reference for the Co-SiC system.

Corundum is an alumina powder with high phase purity and platelet particles shape, normally $(5-10) \mu m$ diameter and $(2-3) \mu m$ thickness. The corundum powder is compacted and sintered to produce a disc sample (25.6mm) diameter and (2.2) mm thickness [97]. The compaction and sintering procedure of the sample result in an axisymmetric texture and a minimum microstrain development and its associated line broadening as well as the absence of crystallite size

broadening [97]. These features make the corundum SRM 1976b suitable for obtaining an approximate instrument profile function (IPF) and allow it to be used in a previous work for the instrumental calibration [97].

After the instrumental effect been convoluted and the line profile corrected, $k\alpha 2$ should be stripped as mentioned in a previous study [98]. Once that done, various analysis can be performed to find the crystallite size and also the internal strain (if available) in the sample. The most common methods analysis are: Scherer (depends on the measurement of width at the half peak (FWHM)), **Figure. 4.7**.

Scherer expression [99]:

Scherer **Equation** (4. 7) is one of the oldest expression that used to estimate the crystallite size by Scherer in 1918. It's usually used for polycrystalline powder samples and does not taking into account the strain effect.

$$\beta = \frac{k\lambda}{d\cos\phi} \tag{4.7}$$

ø: is the peak broadening angle in radian, λ is the wavelength of the radiation, d is the average crystallite size normal to the diffraction plane, and k is a correction factor that depends on many factors: the crystallite shape, crystallite size distribution, and the breadth definition [100]. Depending on the crystallite shape k is given in the range of (0.9 -1.39) [101].

In order to estimate the crystallite size (for comparison of all the produced coatings crystallites size), Scherer equation was used and the numerical constant k assumed 0.9 same as for circle crystallite in this study [100, 102] as the crystal shape of the plated cobalt is unknown.



Figure 4-7: Deconvolution of Ka2 from single diffraction peak [96]

III. Test and analysis

Deposited coatings were prepared by loading them into the XRD sample holder, **Figure. 4.6**, in preparation for analysis with a BRUKER D8 Advance diffractometer. The experiments for all the coatings and the corundum standard SRM 1976b were performed using Cu K α radiation with a 1.5406 Å wavelength employed with a 2 Θ range of 0 – 90° at a step size of 0.010309. Goniometer radius = 25, Equatorial slit = 2.

The nano-SiC (45-55 nm) used was compacted into the XRD sample holder and analysed using the same XRD procedure and conditions. The same XRD experimental details given for the Co-SiC established for the analysis of Co-Al₂O₃ nanocomposites coatings. Instrumental calibration assessed using an internal standard of pure silicon with a particle size of 1-5 μ m. Additionally, pure powders of the Al₂O₃ and PTFE particles used were analysed in order to assign their position in the nanocomposites. For all the prepared coatings, the orientations corresponding to the peak positions for cobalt were found from the hkl-generator of the EVA software using the cobalt lattice parameters a, b, and c of 2.5071, 2.5071, and 4.0686, respectively, and the space group (194). Crystallite size analysis was performed using the EVA software and Maud; the EVA software depends on the Scherer equation to calculate the crystallite size.



Figure 4-8: Sample preparation with XRD sample holder for XRD analysis

4.4 Mechanical Properties Characterization of the Produced Coatings

This section presents the details of the hardness tests that were performed in micro- and nanoindentation to study the hardening of the Co and Co-SiC and Co-Al₂O₃ only. Nanoindentation tests implemented for different nanoparticles were included for comparison with microhardness so as to study the ISE effect. Further, the tests were used to predict the tribological performance of the cobalt and the nanocomposites. Finally, the Co-SiC with nano-SiC 0-8 vol. % performance in tribological applications using pin on disc wear tests was examined.

4.4.1 Microhardness indentation

The coatings' strengths were evaluated from the hardness number of each coating using a Knoop microhardness indenter. The Knoop indenter was used as it gives a precise measurement of the small workpieces that proved difficult using other indenters [103]. In this study, a Mitutoyo model MVK-G1 microhardness meter with a diamond, pyramidal tip was used, and whose geometry is shown schematically in Figure 4.9. The hardness was measured for the cross section of the coatings to avoid the cracks and voids present inside the coatings. In order to allow accurate measurements, two different loads were chosen to assess the produced coatings (10 gf and 25 gf) [104]. Loading values were limited because of the allowed load that can be applied to the coating thicknesses, which ranged between 20-30 µm. All the microhardness results were subsequently obtained using the same experimental conditions. Tests were performed at a loading rate of 0.1 mm s⁻¹ and a dwell time of 10 s at room temperature. The measurements were calculated by averaging ten indents in the cross section of each specimen, leaving a space approximately three times as large as the indentation width, as per Figure 4.10, to eliminate the effect of the plastic deformation surrounding each indent (Chandler and International, 1999). Knoop hardness number (Kgf mm⁻²) is given directly by the following equation [105]:

$$KHN = 14228 \left(\frac{P}{l^2}\right) kgf. mm^{-2}$$
(4.8)

Where *P* is the applied load, and l is the diagonal length.

The hardness of a standard of 705 HV was measured for comparison. The average Knoop hardness of this standard, acquired from the load of 0.025 kgf, was measured to be 917.2 HK25 with a sample standard deviation (SSD) of 30.1 HK25. Only an applied load of 1 kgf or more gave results close to 740 HK, which is comparable to the 705 HV. Because of the high error, the hardness values obtained in this work are only comparable to values from the literature specifically obtained by Knoop micro-indentation hardness tests with a load of 0.025 kgf. Such hardness is denoted by HK25.



Figure 4-9: Knoop indenter geometry and the resultant indentation in the workpiece



Figure 4-10: Schematic of Knoop indentations for the plated specimens

4.4.2 Nanoindentation test

Depth indentation tests (nanoindentation) are used to characterize coating hardness, depth of indentation and elastic modulus. In this work the depth indentation test (nanoindentation) was performed to characterize the coatings' hardness's, depth of indentation, elastic modulus, and to compare nanoindentation hardness with microhardness results. As the indenter was driven into the material, an elastic and plastic deformation resulted at the surface of the material, forming an impression of the indenter shape to a certain contact depth (h_c), as shown in **Figures 4.11** and **4.12**. As the load was removed, only plastic deformation stayed at the sample surface and this allowed an accurate characterization of the elastic and plastic impression in the specimen was calculated as a function of the indenter load as found in literature given in **equation (4.9)** [106] [107]:

$$h_c = h - \varepsilon \cdot \frac{P}{S} \tag{4.9}$$

Where *P* is the maximum load, S=dP/dh is the stiffness (which is calculated after fitting the upper part (50%) of the unloading curve using Oliver and Pharr method) *h* is the total depth of the indentation and ε is a geometrical constant in the range 0.72-1, with ε = 0.75 normally for Berkovich nanoindenter. The contact area in turn for test is determined from the value of h_c and the known geometry of the indenter. For a Berkovich indenter that used in this work, the contact area can be calculated from **equation (4.10)** given below:

$$A(h_c) = 24.5h_c^2 \tag{4.10}$$

Knowing the contact area allows hardness calculation as the indentation hardness is the peak indentation load divided by the projected contact area of the impression:

$$H = P/A_C$$

(4.11)

The specimen elastic modulus is calculated by measuring the "stiffness" of the contact, [106] as in **equation (4.12)**:

$$E_r = \frac{\sqrt{\pi}}{2} \cdot \frac{S}{\sqrt{A}}$$
(4.12)

where E_r is the reduced modulus that takes into account both the indenter (i) elastic modulus and specimen (s) elastic modulus given by:

$$\frac{1}{E^{\rm r}} = \frac{(1 - v_S^2)}{E_S} + \frac{(1 - v_i^2)}{E_i}$$
(4.13)

So, three parameters are needed to calculate the hardness and elastic modulus: the peak load (P_{max}) , the depth at peak load (h_{max}) and the initial unloading contact stiffness (S_{max}) .



Figure 4-11: A schematic for load- displacement in nanoindentation



Figure 4-12: A schematic represent a section through the nanoindentation, (Oliver and Pharr, 1992)

I. Indenter type

The nanoindentation test was performed using a G200 nano-indenter, which was controlled using the Test Works 4 software. The software uses the Oliver and Pharr analysis method [106] for hardness and Elastic modulus calculation. A pyramidal Berkovich indenter with a 20 nm diamond tip, a face angle of 65.27° and a tip radius in the range 50-100 nm was used. The indenter is provided with environmental isolation which consists of a vibration table and a thermal-sound-insulated vibration isolation cabinet. In addition, all measurements were performed at night to eliminate general vibration effects.

II. Test procedure

The experimental input parameters were chosen for the indentation measurements as per **Table 4.6**. Ten repeated measurements at the centre of the coatings' cross-sections were performed to increase the validity of the results with a 5 μ m located spacing to avoid the deformation influence in the region surrounding each indentation. Hardness and modulus of elasticity were calculated from the load-displacement data for each indentation by the Oliver and Pharr [75] method.

Name	Value	units
Allowable drift rate	0.050	nm s ⁻¹
Load Rate Multiple for Unload Rate	1	-
Maximum Load	100	mN
Number of Times to Load	5	-
Peak Hold Time	10	S
Percent to Unload	100	%
Time to Load	15	S
Poison Ratio	0.3	-

Table 4-6: Required input for nanoindentation test

4.4.3 Tribological performance

The tribosystem usually consists of four elements: a solid body; a counter body; an interfacial element; and an environment.

Wear behaviour of the coatings with low and high volume fractions of particle inclusions were investigated, considering inclusions in the range of 1-8 % .vol, after which they were compared with the pure cobalt coatings produced under the same conditions to study the effects of oxide/hydroxide availability.

I. Sliding wear test setup

The dry sliding wear test (pin-on-disc) using Bruker's Universal Mechanical Tester CETR-UMT-2 was used to study the wear and frictional behaviour of the samples. The UTM allows the actual dynamic normal force, frictional force and coefficient of friction and depth of wear to be monitored during the test. The basic UMT system consists of a computerized control unit, software, and the testing unit, **Figure 4.13**, where the testing unit is presented from a previous work [108]. Pin on disk is one of the test that can be performed using the UMT machine. The pin-on-disk system consists of a friction/load sensor, rotational drive, specimen holder and specimen. The rotary drive allows speeds from 0 to 5000 rpm and loads from 0 to 20 N in order to make the force measurement more accurate, as results might not otherwise be sufficient to build a complete, understandable picture as to the dynamics of the friction, wear or the failure of the coatings. The sensor is suitable for normal and friction load, whilst the vertical carriage controller controls the load and keeps it constant during the test. A PC-based motor controls

the vertical (z) and lateral position (y) to adjust the sliding radius at the stationary the ball contacts the rotating lower disc (specimen).

II. Sample preparation and electroplating

A steel disc substrate (38 mm diameter and 5mm thickness) was used for the test. Surface pretreatment was carried out by polishing and grinding the substrate before the electroplating to produce as smooth a surface as the steel substrate surface used in section 4.2.1. Silicon carbide papers (180, 360, 400, 600, 800, and 1200 grit) were used sequentially for the grinding, then all samples were polished with diamond abrasive (6 μ m and 1 μ m) and kept in preparation for electroplating.

The same bath as that used in section 4.1 was used for the electroplating but with a size of 1 L to compensate for the ion content, i.e., to avoid the concentration effect.

III. Test procedure

An alumina ball (99.9%) with a 10 mm diameter was used as a counter body. The ball had an elastic modulus of 400 GPa, a 0.21 Poisson Ratio (v) and a 45 N 81 Rockwell hardness. The disc diameter was 38 mm. Using the installed software, the procedural steps were created according to the required conditions. A low load of 5 N was applied at a speed of 0.1 ms⁻¹ and a 500 m distance for all experiments; a track diameter of 25.4 mm was chosen. The initial mean contact pressures under the chosen load 0.6 GPa was calculated (assuming Hertzain contact between a sphere and a plane) and using typical values of Young's modulus and Poisson ratio for steels of 213 GPa and 0.29 respectively. The sliding distance was fixed at 500 m, with a sliding speed of 0.116 ms^{-1} and a wear track diameter of 28 mm. After each test, resultant data for the friction force F_x, normal force F_z, time, and coefficient of friction were generated automatically and saved onto the computer. Debris were taken from the sample surface in the region of the wear track and the surrounding area, and were kept for subsequent characterization. Friction is governed by the surface interaction in moving contact. The friction force, F, and coefficient of friction, ω , were automatically generated by the software. Friction force was calculated with the available software according to classical theory as per the following [109]:

$$F_F = A\tau \tag{4.14}$$

And the coefficient of friction is given as:

$$\omega = F/W \tag{4.15}$$

$$= A\tau/W \tag{4.16}$$

Where *F*, *A*, τ , and *W* are the friction load, real contact area (sum of area of contact asperities), the effective shear strength of contacts, and the applied normal load, respectively.

The wear volume, as calculated from the 3D microscope, was used to calculate the wear rate, which is simply the wear volume divided by the sliding distance, V/l, where V is wear volume lost in (mm³) and l is the sliding distance in (m). It should be noted that the measurement were implemented under the assumption that the wear behaviour is none varied during the test, which is practically cannot be happened in reality. As the measurements are taken at the end of the test this will not be possible to measure the change in the wear behaviour.



Figure 4-13: Schematic image of the Bruker Universal Mechanical Tester (UMT) with the rotary drive (shown on the right) used for wear test performance (Ivanov et al, 2012)

IV. Surface characterization

The morphology of the sample surface was studied before and after the wear test using infinite focus microscopy (IFM), Alicona production. Infinite focus microscopy is an optical 3D micro-coordinate system used to examine surface morphology. IFM is based on an optical technology

that delivers more than 100 million measurement points at the measurement density. It has the ability to measure a large areas and volumes of surfaces. The vertical resolution of IFM is up to 10 nm at 100x magnification and 250 nm at 10x magnification. All relevant surface features are measured using only one multifunctional measurement sensor.

CHAPTER 5: MICROSTRUCTURAL CHARACTERISATION OF Co-SiC

5.1 Introduction

The behaviour of a particular nanocomposite system is highly dependent on the nature, number and distribution of embedded nanoparticles and their interaction with the matrix. Hard metal matrix nanocomposite electroplated deposits containing hard SiC nanoparticles were shown to have a high resistance to abrasive wear compared to pure metals, like nickel [18, 110] and Cr [111]. Review papers showed the lack of investigation of the tribological behaviour of Co-SiC nanocomposites [18-20, 112, 113].

A preliminary work [78] on Co-SiC by Weston et al, using the proposed PRP and anionic surfactant with varied Sodium Dodecyl Sulphate (SDS) from (0 - 1 g l⁻¹), the electrophoretic effect was explored more fully. The results showed an optimum SDS content with cathodic time to achieve a well-dispersed distribution of SiC in the cobalt matrix, Figure 5.1, Figure 5.2. It was found that the volume fraction of the SiC particles increased with decreasing duty cycle (particularly in this study, cathodic time), as can be seen in Figure 5.1. This was accompanied by the formation of cracks at the interface area between the coating and the substrate with the low duty cycle that occur due to the dissolution over the first few anodic cycles of the PRP, as was shown by SEM images of the cross section of the deposit. The surfactant content effect was also investigated for the deposition of nanocomposites, the results of which showed that coatings produced with no SDS showed a negligible effect due to the use of PRP compared to DC, and for different t_c with a SiC volume fraction up to 4%. Addition of SDS resulted in enhanced particle content that increased further with increasing SDS content up to 0.6 g l⁻¹, after which a decline in particle content could be seen. The highest volume fraction of the particles was 18% at $t_c = 30$ s and 0.6 g l⁻¹ SDS. This was explained as follows: increasing surfactant content increases adsorption onto the particles, but above a certain limit a larger repulsion force will be created between the surfactant layer near to the cathode and the approaching particles. The repulsion force resulted when the micelle* molecules available in the bath reach a critical concentration.

^{*}Micelle: is a surfactant molecule aggregate that dispersed in the bath colloid. Typically the micelle forms an aggregate with hydrophilic head region in contact with the surrounding solvent.

Hence, it will impede the particles from reaching the working electrode and their encapsulation. Previous studies proposed that when micelle concentration reaches a critical value in the electroplating bath, further increase in the surfactant will be not effective [114]. In other words, they tended to react together as it disrupted the even dispersion of nano-particles, facilitated their agglomeration, and reduced their incorporation [115]. Therefore, there was an optimum concentration $0.4 \text{ g } 1^{-1}$ for SDS for this system, beyond which dispersion quality of nano-particles in electrolyte, and in turn the distribution quality of nano-particles in coatings, were lowered and this made the properties of the coatings poor.



Figure 5-1: Volume fraction % variation of the nanocomposites (Co-SiC) accounting for the effect of SDS content and cathodic time taken from previous data [78]



Figure 5-2: Cross sectional back-scattered images of Co-SiC electrodeposited nanocomposite at different magnifications from preliminary work [78]

This chapter will address the production of those nanocomposites Co- SiC coatings and compare them to the pure cobalt that produced in the same plating conditions. An anionic surfactant content, SDS $(0.2 \text{ g} \text{ l}^{-1})$ nominated as it afforded high particle incorporation and good cross-sectional properties as well as high hardness confirmed by microhardness measurements, **Figure 5.3**. Additionally, no cracks and brittleness was found.



Figure 5-3: Microhardness of the nanocomposites Co-SiC against the SiC vol.% from the previous work [78]

In order to eliminate the hydroxide formation during the anodic pulse in PRP cobalt bath with gluconate complexing agent used to produce the Co-SiC. Gluconate electrolytes are non-toxic and it is suggested that they cause no adverse effects on the environment [116]. As in the presence of sodium gluconate in acidic solutions, Weston et al [116] summarised that gluconate ions forms complexes with Co^{2+} ions and reduces the availability of free Co^{2+} . Hence, the formation of $Co(OH)_2$ will be eliminated in PRP plating. Nano SiC with average particle size of 50 nm used.

Firstly, pure cobalt with 0.2 g 1^{-1} will be examined in comparison with the Co-SiC 5 g 1^{-1} SiC. To enrich the particle inclusion to gain the highest particle volume fraction possible, the effect of particle loading in the bath is also considered, with ranges from 5 to 20 g 1^{-1} . Microstructural characterization of the deposits will be assessed including the cross-sectional SEM images and EDX chemical composition analysis. XRD analysis to study the texture of the coatings and the effect of particle encapsulations on crystallite size and crystallite size distribution. TEM bright field images for coatings with the highest particle contents to show the particles dispersion, spacing between particles, crystallite size analysis to support the previous XRD analysis. Also,

metal nanoparticles interaction can be recognized. Finally, the PRP with SDS anionic surfactant technique assessment is presented from the cathode current efficiency and particles deposited per cycle.

5.2 Results

The first part of the results will concentrate on investigating the microstructural characteristic of the coatings from cobalt baths of the pure cobalt and Co with nano SiC 45-55 nm average diameter and particles loading is 5 g l⁻¹. Both coatings are with 0.2 g l⁻¹ SDS content B1 of pure cobalt and B2-a of Co-SiC and 5 g l⁻¹ were plated to give full coverage insight of used technique on the surface topography, cross section appearance, roughness, particles dispersion, coatings chemical composition, and crystallite size. The next section concentrates on the assessment of the technique with different particles loadings in the range 5-20 g l⁻¹.

5.2.1 Microstructural Analysis of Co-SiC and Pure Co coatings with different duty cycles

I. Field Emission Gun Scanning Electron Microscopy FEG-SEM

Scanning Electron Microscopy (SEM) analysis was used to determine particle distributions and the presence of voids, porosity and/or oxygen from the cross section observation of the produced coatings. Cross section SEM images of the coatings from PRP, $t_c = 30$ s showed coatings high particle content distributed through cobalt matrix but with poor adhesion to the substrate, Figure 5.4-i. The poor adhesion is due to the dissolution of the coatings at the few initial anodic cycles at the start of the electroplating. Coating with $t_c = 60$ s performed similarly but with a better adhesion compared to the coating with $t_c=30$ s, Figure 5.4-ii. Also, microcracks can be seen in the area close to the substrate that could be extended to the coating due to the selective anodic dissolution of the steel substrate that more readily dissolves than the Co, as it is more active. Pits are formed accordingly. To overcome the problem of the dissolution, a thin layer of a deposit can be Galvanostatically plated at the initial time of the electroplating with DC. This is known as a strike to ensure the formation of a thick enough layer to prevent Fe dissolution [117] [38]. Hence, in this work a strike for 300 s and approximately 1 µm thickness was electroplated before starting the PRP plating. However, this was found to be insufficient to eliminate the dissolution of the Fe at the start of the plating for all coatings with low duty cycle.



Figure 5-4: Coatings with poor coating- steel adhesion at low duty cycle: i) Co-SiC with t_c= 30 s, ii) Co-SiC with t_c=60 s

Another attempt was made by plating with longer strike time of 600 s for bath 2 before the PRP with 2 μ m depositing thickness. SEM cross section of the produced coatings presents promising results, where coatings with good coating- substrate adhesion for the coatings with t_c= 60 s produced successfully with no apparent pitting and dissolution, **Figure 5.5 i**. This is an improvement of the cross section coatings produced by PRP compared to the coatings produced from earlier works [7, 16] that suffered from the same issue. Coating t_c = 30 s possessed some poor adhesion dissimilar to the coating at t_c=60 s and was excluded for the rest of PRP in this work and only use cathodic times of t_c= 60 s, 90 s, 120 s and 3600 s with a strike for 600 s at the beginning of the electroplating were considered further.

Field emission gun scanning electron microscopy FEG-SEM cross-sections of all the coatings with different duty cycles up to 1 showed excellent adhesion to the substrate with no pits through the coatings for the different t_c employed, as shown in **Figure 5.5**. High magnification cross section images for the electroplated nanocomposites from Cobalt bath B2 –a with 5 g l⁻¹ SiC and DC presumably showed low particle contents with some agglomeration through the deposit, **Figure 5.5 v**. The cross-section showed particles dispersed in higher amounts at the area close to the substrate, decreasing in frequency with increasing distance from the substrate. This is accompanied by a smooth surface finish at the top of the coating. The particle dispersion mechanism in DC was explained previously [16] as follows. The use of anionic SDS confers a negative charge on the nano particles which should provide an electrophoretic effect on the particles away from the working electrode during the cathodic phase. In DC the SDS is claimed

CHAPTER FIVE: MICROSTRUCTURAL CHARACTERISATION OF Co-SiC

to behave in a similar way to the cationic surfactant as it is able to disperse the particles in the plating bath but it will not promote their attraction to the cathode during deposition.

Coatings produced with PRP showed even distribution of the nano-SiC particles through the coating thickness which is in the range of 19-47 μ m for different t_c . Less particle agglomeration can be seen compared with DC coatings, **Figure 5.5**. The coatings thickness decreases slightly with decreasing duty cycle, with negligible effect on surface roughness compared to the DC coating.











Figure 5-5: SEM -BSE cross section of Co-SiC with 5 g l⁻¹ nano-SiC showing adhesion of the coatings to the substrate for low and high magnification for coatings with different t_c with low and high magnification for each duty cycle: i) t_c =60 s, ii) t_c =90 s, iii) t_c =120 s, iv) DC with low magnification, v) DC with higher magnification showing less particle content compare to the PRP

II. Energy Disperse X-ray Spectroscopy EDX

EDX analysis confirmed the low particle content of DC coating from bath 2 of Co-SiC and 5 g l⁻¹ from an average of the whole coating thickness. The atomic weight percent obtained was converted into vol. % and plotted against the cathodic time again for all produced coatings. DC coating performed 1.8 vol. % content and found to be similar to the content from previous studies for $t_c = 25$ s and 30 s [16, 62]. These studies investigated DC and PRP co-deposition of nanocomposite Cu-Al₂O₃ and Co-WS₂ systems respectively. Another study using DC, pulse electroplating PE, and PRP found the volume fraction of nanoparticles included was highest for PRP compared to the other techniques used [118].

EDX results of the PRP coatings showed higher particle contents compared to the DC coatings and are ranging 4-9 vol. % for the different t_c , **Figure 5.6**. The increase in particle content with PRP compared to the DC was confirmed in a number of works on PRP [7, 16, 119]. This is attributed firstly to the effect of PRP in selectively removing some of the deposited cobalt metal in the anodic pulse and led to an increase the particle content accordingly as was shown in [7, 62, 119]. Secondly, the effect of the mechanism of the PRP and SDS that conferred the particle the negative charge and attracted them into the working electrode in the anodic pulse as proved in Weston et al [16]. Higher particle contents for PRP coatings can be seen, particularly with cathodic time $t_c = 60$ s where 8.7 vol. % is observed comparable to 10.4 vol. % in the former work by Weston [16]. A reduction in volume fraction is seen at $t_c = 90$ s and 120 s, **Figure 5.6**, in a similar way as for the preliminary work on Co-SiC.

EDX analysis was also performed to investigate the content of oxygen in the coatings. The results showed the concentration of oxygen reaches to 7.6 at. % in DC, which is quite a high value. Oxygen content was ranging between 5.1-5.3 at. % for the coatings from PRP throughout the whole cross section of the coatings, **Table 5.1**. However, no oxygen was seen through the coating cross section in FEGSEM images. Hence, the results will not be considered.



Figure 5-6 SiC content of Co-SiC nanocomposite coatings produced by PRP with different duty cycles, with fixed t_a and variable t_c .

t _c /s	60	90	120	DC
Co / at. %	91.26	89.66	91.33	93.12
Si /at. %	3.56	2.67	3.43	1.23
O / at. %	5.32	7.67	5.1	5.65

Table 5-1: EDX analysis for Co-SiC with 5g.l⁻¹ SiC

III. Surface topography

The coatings morphology studied with Secondary Electron (SE) SEM on the surface of the coatings produced via DC. **Figure 5.7-i** showed cobalt particles distributed in different directions (some are highlighted with red arrows) with 2μ m in longitudinal direction and 0.7 μ m in traverse direction the inclusion. Some agglomerated nano-SiC particles (highlighted with blue arrows) can be seen embedded in cobalt matrix. For the other layers, **Figure 5.7- ii, iii, iv**, produced from PRP, it can be seen the selective dissolution resulted in a smoother cobalt surface and no noticeable SiC particles.



Figure 5-7: SEM images of coatings from bath 2 with 5 g. l⁻¹ SiC and different duty cycles, i: 1, ii: 0.71, iii: 0.81, iv: 0.86

IV. X-Ray Diffraction (XRD)

XRD patterns for all the deposited pure Co and Co-SiC coatings with 5 g 1^{-1} SiC showed anisotropic hexagonal closed packed (hcp) structures with two peaks with no peaks for oxygen, **Figure 5.8**. Former studies confirmed the appearance of electroplated cobalt as hcp crystal structure with high pH [16, 120, 121]. These peaks were assigned to the (100) and (110) orientations using the (hkl) generator in EVA software. No significant peaks were seen for the SiC nanoparticles. Previous work on Co-WS₂ using SDS surfactant and PRP with the same chemical composition of the cobalt bath and similar pH and plating condition showed a similar main peaks orientation in the directions (100), (110), as well as (200), (101) that are not present in this work. Peak broadening can be seen in all the Co-SiC compared to the pure Co, **Figure 5.9**. This is due to SiC adsorption on the cathode surface which increases the available area for

CHAPTER FIVE: MICROSTRUCTURAL CHARACTERISATION OF Co-SiC

the nucleation of the cobalt crystallite [24, 122]. This is accompanied by an intensity decrement of the Co peaks.



Figure 5-8 XRD pattern for pure Co with different cathodic time



Figure 5-9: XRD pattern for Co-SiC with different cathodic times.

CHAPTER FIVE: MICROSTRUCTURAL CHARACTERISATION OF Co-SiC

Grain size analysis performed using EVA software were based on Scherer calculations of the grain size [99]. By importing the reference sample file, which is corundum for these nanocomposites, and the experimental XRD pattern for the selected batch of the Co and Co-SiC coatings k α 2 was removed firstly (stripped) with the value measured, presented in **Table 5.2**. The instrumental broadening was found by working out the closest peak of the cobalt to (100) or (110) and the imported corundum reference, and using **Equation 4.10** assuming that the peak shape is Cauchy.

The calculated grain size demonstrates the change in grain size of pure cobalt and Co-SiC with different t_c and with different particle inclusion content. Grain size for the two-different plane directions (100) and (110) for pure Co and Co-SiC are presented against t_c in **Figures 5.10** and **5.11** respectively. The plots showed the grain size of pure Co produced by PRP and DC did not change noticeably in both (100) and (110) planes and are ranging 80-89 nm in (100) and 67-69 nm in (110).

Also, no noticeable change in grain size for all the Co coatings produced by PRP with different t_c , and the cobalt species formed in different t_c did not affect as well. The nanocomposites Co-SiC showed a smaller grain size in the (100) and (110) planes compared to the pure cobalt of about (9 -30) nm grain size reduction. This assumption takes into consideration the calculation of the grain size using Scherrer equation, which is approximate with some error. However, these approximate calculations are used for all the coatings, which means that it can give an indication about the grain size reduction due the nanoparticles inclusion.

Co peak [° 20]	corundum (Al ₂ O ₃)	Instrumental line	
	peak used [°20]	broadening [°]	
41.59 (100)	39.60	0.059	
75.90 (110)	76.06	0.075	

Fable 5-2 : Instrumental line broadening	, Values obtained after	stripping Ka2
---	-------------------------	---------------



Figure 5-10: Grain size of pure Co, Co in Co-SiC with different duty cycles in (100) plane estimated using Scherer equation



Figure 5-11: Grain size estimated using Scherer equation for Co, Co matrix in Co-SiC nanocomposite in 110 plane with 5 g l⁻¹ SiC loading and with different duty cycles.

To demonstrate the change in grain size for all coatings produced by PRP and DC and also the effect of t_c , SiC vol. % plotted against grain size, **Figure 5.12**. A slight change in grain size of the nanocomposites with different t_c can be seen, from 76 nm to 62 nm in 100 peak and from 67 to 54 in (110). This variation proved that there is good dispersion of the particles through the metal matrix as it results in smooth decline in the cobalt grain size. The variation is attributed to the variation in the dispersed particle vol. % for each t_c .



Figure 5-12: Grain size variation of Co matrix with SiC vol. % for Co-SiC 5 g l⁻¹ SiC in (100) and (110) planes.

V. TEM

A selected electrodeposited sample of B2-a, of Co-SiC and t_c = 60 s that possessed high particles inclusion 8.7 vol. % was selected for TEM analysis to investigate the particles dispersion that achieved by PRP and SDS from the lowest duty cycle.

Bright field transmission electron microscopy TEM images for the specimen showed nano SiC particles with spherical shape known from previous works [123, 124], Figure 5.13 shows a TEM image for 50 nm diameter β -SiC used in a previous work [124] with a spherical shape. In the current work Figure 5.14 showed the nano SiC embedded through the cobalt matrix. A decent dispersion of nano-SiC particles, Figure 5.14, i with some agglomerations through the selected area of the coating can be seen Figure 5.14, ii. The dispersed particles average size ranges from 35-100 nm. The results were compared to a previous work on co-electrodeposition of nanoparticles via PRP and DC into metal matrix [7, 17]. The study focused on the electrodeposition of nano Al₂O₃ with 30nm diameter in a copper matrix using a rotating disc electrode and supported by ultrasound physical agitation. They suggested that PRP produced a coating with less agglomeration compared to the DC coating. The study compared TEM images for both DC and PRP coatings to support that finding, see Figure 5.15. The low particle agglomeration was explained to be resulting from using PRP and ultrasonic agitation. Comparing the TEM images of the current work with TEM from that previous work of PRP coating reveals that nano SiC is less agglomerated. This supports the positive effect of the chemical activation dispersion resulted from the surfactant additionally to the ultrasonic effect. Hence, it suggested that the PRP technique used with SDS and with a suspension of particles inside the electrolyte can be successfully used to disperse small nanoparticles and avoid the agglomeration effect.



Figure 5-13: TEM image of spherical nano β-SiC particles from an earlier work, (Heidari, et al, 1992)


Figure 5-14: SiC nanoparticles dispersion with some agglomeration in i and ii



Figure 5-15: Bright-field, cross-sectional TEM image: i) A DC-plated Cu–Al₂O₃ composite on a rotating disk electrode with a wide particle size distribution, ii) A PRC-plated Cu–Al₂O₃ nanocomposite onto a rotating disk electrode showing Al₂O₃ nanoparticles dispersion with particles of 100 nm [7, 125].

The spacing between the particles were worked out from the TEM bright field images in **Figure 5.16.** The results confirmed the dispersion of the nanoparticles, where a decent dispersion was

noticed with spacing between particles, L_p , ranging between 100-250 nm. Similar spacing can be seen in **Figure 5.14**.

According to the literature, there is gap in knowledge for the characteristic of the metal matrix and the nanoparticles interaction [19]. TEM characterization in this work enabled us to study this interaction. The TEM bright field images showed a good metal- nanoparticles interaction, **Figure 5.16** with no porosity seen.

Another prepared specimen analysed by bright field image showed some grains boundaries through a thick section that was identified as Co grains, as the coating consists of Co and SiC particles. A previous study showed Co grain size in TEM [126] for the electroplated Co by DC and with pH = 4 to be 400-500 nm, comparable to the noticed grain in the current work, **Figure 5.17 i, ii**. Sketching the recognized grain boundaries, **Figure 5.18 i , ii** gave an indication that Co matrix grain sizes are in the range 35-101 nm for coating produced by PRP and tc = 60 s. Further analysis is given in **Figure 5.19** to show both the nano SiC particle diameter and the grain boundaries of Co. These results are approximately similar to the calculated grain size from XRD analysis shown in the previous section.



Figure 5-16: Highlighted SiC nanoparticles with uniform dispersion through Co with highlighted nanoparticles and measured spacing between particles



Figure 5-17: Electroplated Co and Co-SiC produced in an earlier and current work showing Co grains and grain boundries i) TEM image of electroplated Co produced by DC, [126], grain size 400-500 nm, ii) TEM image of Co-SiC in this work PRP, tc= 60 s, Grain size 35-100 nm



Figure 5-18 Comparison of i) original TEM image with grains boundaries of Co matrix with, ii) Schematic representation of Co grains boundaries



Figure 5-19: SiC nanoparticles with diameter = 32.3 nm dispersed within the grain of Co matrix as measured in TEM and without agglomeration

5.2.2 Microstructural analysis of Co-SiC with Different Particle Loadings and Sizes

The previous section considered a Co-SiC coating with a bath loading of 5 g l⁻¹ SiC and a particle size of 50 nm, and a pure Co film. This showed that Co-SiC coatings were successfully produced by the PRP and anionic surfactant SDS technique with particle inclusion higher than coatings produced by DC and with a similar trend compared to the previous work [78]. This part aims to investigate the mechanism of PRP and 0.2 g l⁻¹ SDS for Co-SiC with higher particle loadings using the same particle size 45-55 nm. Additionally, the co- deposition of a smaller SiC particle of 30nm will be addressed. Electroplating by DC will not be considered anymore in this section and the coatings will be produced only by PRP and using the same plating parameters for Co-SiC with 5 g l⁻¹ of t_c= 60 s, 90 s, and 120 s.

I. FEG-SEM

The cross section observations of Co-SiC with 5-20 g l⁻¹ SiC coatings were performed with FEG-SEM in back scattered mode (BSE) at low magnification to clarify coating adhesion to

the substrate surface. Also, the FEG-SEM used to analysis the particles dispersion through the coatings thickness at different particles loading, and the surface roughness. In addition, high magnification BSE analyses were accomplished to investigate particle agglomeration with different loadings. Coating from bath Co-SiC of 5 g 1⁻¹ SiC loadings is also presented for comparison. The coatings from different t_c= 60, 90 s and 120 s behave in similar way and hence only coatings of t_c = 60 s are presented to illuminate the effect of particle loading in the bath parameter.

The cross section images of all the coatings with low magnification show good coating adhesion to the steel substrate with no microcracks at the interface area. An increment in the particle content with increasing particle loading in the bath can be seen with good particle dispersion, **Figure 5.20**. This is accompanied by rougher surfaces for the films from higher particle loadings, but with a similar range of coating thicknesses to that obtained for 5 g l⁻¹ SiC in the range 28 - 37 μ m. Higher particle inclusion for coatings produced by DC was observed in previous work for electrodeposited Ni–Al₂O₃ composite layers from a nickel electrolyte bath with 40 g l⁻¹ alumina but with no surfactant used [118]. This was expected to be result in agglomeration facilitated by the increased particle collision probability [22]

BSE with high magnification demonstrated no noticeable agglomeration with particles loading up to 15 g l^{-1} SiC, **Figure 5.20 i, ii**, **and iii**. Few agglomerated particles observed for high loadings of 20 and 25 g l^{-1} SiC and less uniform dispersion, **Figure 5.20 iv, and v**.







Acc V Spot Det WD 5.00kv 5.0 BSE 8.0 100nm











Figure 5-20: BSE images SEM, high magnification cross section of the Co-SiC, t_c = 60 s with different loadings at two different magnifications: i) 5 g l⁻¹, ii) 10 g l⁻¹, iii) 15 g l⁻¹, iv) 20 g l⁻¹, v) 25 g l⁻¹

II. Energy Disperse X-Ray Spectroscopy

Particle contents were analysed with EDX for the coatings cross section to reveal how much particle content increment can be achieved with particle loading in baths by PRP and 0.2 g l^{-1} SDS, and assessing how well distributed the particles will be. The atomic weight percent obtained was converted into vol. % and plotted against the cathodic time for all produced coatings and compared to the vol. % of coatings produced in the previous section with 5 g l^{-1} SiC, **Figure 5.21**.

A slight increment in vol. % for coatings 5-15 g l^{-1} at t_c = 60 s throughout the cross section of the coatings is observed. While coatings produced with $t_c = 90$ s and 120 s showed a higher particle increment that reaches up to 7.9 vol.% at $t_c = 90$ s compared to 4.7 vol.% for 5 g l^{-1} SiC particle loading, and up to 9.1 % at $t_c = 120$ s with 15 g l^{-1} SiC compared to 6.4 % with 5 g l^{-1} SiC. Also, it can be recognised that the particle increment in coatings produced by high duty cycle is higher than that for coatings with low duty cycle. At 20 g l^{-1} particle loading in the bath, all the coatings experienced no apparent increment in particle content. The overall trend of the particle inclusion with different t_c is still expected. The results suggested a saturation steady state might be achieved at 20 g l^{-1} . Further particle loading at 25 g l^{-1} SiC was implemented with $t_c = 60$ s to investigate the saturation effect. The results exhibit a particle volume fraction of 8.3 %, which is approximately similar to the vol. % attained at 20 g l^{-1} SiC. Increasing the particle loading further is expected to result in a decline in particle inclusion due to the expected high density, high viscosity and dispersion instability at high particle loadings

in the bath as mentioned in an earlier study by Tudela. et, al [50] and due to the decreased effect of the electrophoretic provided by the SDS.



Figure 5-21: SiC volume fraction (%) calculated from EDX with different t_c for Co-SiC with 0.2 g l⁻¹ SiC: i) 5 g l⁻¹, ii) 10 g l⁻¹, iii) 15 g l⁻¹, iv) 20 g l⁻¹, v) 25 g l⁻¹

The obtained EDX results from different tc can be explained by considering the dispersion of SDS throughout the plating bath. At any one time there will be a three way equilibrium between micelles, free SDS and SDS adsorped onto SiC nanoparticles. This will generate a number of SDS molecules per particle. The quantity of SDS has been shown to strongly affect the particle density in the coating. As more particles are added to the bath, the SDS is dispersed across a greater surface area, hence decreasing the mean number of SDS molecules per nanoparticle and diminishing the number of particles attracted to the working electrode during the anodic step. At the same time, increasing the number of paticles in the bath increases the probability of interation and capture at the surface. These two factors combine so that doubling the number of particles in the plating bath significantly increases the particle content of the coating. The supply of particles to the available surface has become saturated, hence further addition of particles on the bath has no further effect on particle incorporation.

III. XRD

XRD patterns for Co-SiC with different particle loadings in the range 5-25 g l⁻¹ showed cobalt hcp peaks at (100), (002) and (110), which indicates a distribution in crystallographic orientation, **Figure 5.22**. Increasing the particle loading results in a negligible effect on the peak intensity in the (100) and (002) directions and (110). No recognized peak for the SiC can be seen for all the coatings.



Figure 5-22: XRD pattern of Co-SiC at t_c = 60s with different particle loadings of 5-25 g l⁻¹ SiC

Grain size calculations using the Scherer **Equation 4.7** for the coatings with different particle loading in the bath are presented against the cathodic time in both directions (100) and (110) in **Figure 5.23**. The overall results for all coatings showed no noticeable change in the crystallite size with changing the volume fractions of SiC in the range of 1.8% - 10% for the (100) and (110) directions, as shown in **Figures 5.23**. However, for each plane direction a slight reduction in grain size can be recognized for the coatings produced from baths with particle loading of 5-15 g l⁻¹ SiC and different t_c. While coatings from bath 20 g l⁻¹ with different t_c showed no apparent reduction.



Figure 5-23: Crystallite size distribution of cobalt matrix with different particles vol.%

5.3 **DISCUSSION**

5.3.1 Mechanism for Co-SiC co-deposition with different particle loadings

SEM cross section image results of the first set of the electroplated nanocopmosites coatings of DC and PRP produced from bath B2-a confirmed the higher particle content in all coatings of PRP compared to their content in coatings of DC. The nanoparticles are dispersed uniformly throughout the whole coating. This was confirmed by TEM analysis for the PRP coating with cathodic time of 60 s. No agglomerated particles were observed through the cross-section of the deposits with 5 g 1^{-1} SiC. While in coatings produced by DC, the nanoparticles are found to disperse in higher content at the area close to substrate than the area away from the steel substrate with some noticeable agglomerated particles. EDX analysis confirms the higher particle content in coatings produced by PRP and the lower content in DC coatings. The higher content achieved by PRP with t_c = 60 s and the less vol. % achieved for DC coatings followed by the coatings produced with higher tc and duty cycle. Additionally, the promoted particle content by PRP and SDS was found to be effective in impeding the cobalt grain size in XRD analysis.

Increasing particle loading in the bath was expected to increase the particle inclusion in all coatings up to certain value then a reduction reached due to the saturation stage. The saturation resulted in coatings with agglomerated particles due to the rise of the collision probability as have been mentioned in previous studies [127, 128]. However, the results showed that coatings with only higher cathodic times demonstrated that effect. Coatings with $t_c= 60$ s did not experience that effect and the most elevated particle volume fractions for the 60 s coatings were reached at particle loadings of 10-15 g l⁻¹ of 9.1 vol. %. This is a similar value to the volume fraction of 8.7% obtained for the shortest t_c with 5 g l⁻¹ SiC. This indicated that 0.2 g l⁻¹ SDS only promotes 8 - 9 vol. % approximately. The reason of such behaviour explained as the following:

Doubling the particle content in the bath resulted in reducing the SDS molecule per nano SiC particle, which resulted in reducing the particle suspension in the electrolyte and decreasing the nanoparticle negative surface charge and at the same time the particles tend to agglomerate. Less particles will be encapsulated in the anodic pulse due to the reduction in the effect of electrophoresis. While at the cathodic pulse the particles will be important to confirm such behaviour. Further increase in particle loading will diminish the PRP and SDS mechanism effect and increase the mechanical entrapment effect, resulting in coatings with more agglomerated particles with uncontrolled dispersion. This effect was witnessed in cross section images of coatings from bath with 20 g 1^{-1} SiC and was confirmed by EDX. XRD analysis also confirmed that there were no noticeable change in grain size for those coatings.

The calculated SiC vol. % and the coating thickness was used to calculate the metal deposited per cycle for all coatings produced by PRP. Metal deposited per cycle is plotted against particle vol. % and compared to the previous work [16], **Table 5.3** and **Figure. 5.24**. High particle vol. % and low deposited metal per cycle for the lower t_c for coatings from B-2a with 5 g l⁻¹ SiC were observed. This is similar to the other coatings from B- 2b-d but with no significant change in particle vol. %. Generally, nanoparticle loadings in the bath produced an acceptable trend compared to the previous work, but with limited increment in particle content.

Previous work on the mechanism of nanocomposites production by PRP [7] and PRP with anionic surfactant [16] suggest that the shortest t_c deposited a higher content of nanoparticles per metal thickness.

Bath	t _{c/}	t _{a/}	Ic	Ia	No.	th/	SiC	Co	Cathode
	S	S	$A.dm^{-2}$	A.dm ⁻²	cycle	μm	vol.%	$M_{dep}g$	Efficienc y%
2a	60	10	-4	8	60	29.4	8.72	0.09875	65.31958
	90	10	-4	8	40	34	4.7	0.11735	69.45877
	120	10	-4	8	30	30.4	6.34	0.10381	57.70647
2b	60	10	-4	8	60	25.0	8.1	0.08201	55.47274
	90	10	-4	8	40	34.9	7.47	0.11827	69.59038
	120	10	-4	8	30	33.0	7.44	0.11344	61.92309
2c	60	10	-4	8	60	25.3	9.16	0.08491	57.17445
	90	10	-4	8	40	33.4	7.99	0.11283	65.65634
	120	10	-4	8	30	34.3	8.27	0.11561	64.28167
2d	60	10	4	8	60	28.8	8.52	0.09691	64.16236
	90	10	4	8	40	32.9	7.86	0.1112	65.10955
	120	10	4	8	30	33.4	8	0.11279	62.33977

Table 5-3: Calculated deposited mass and cathode efficiency of all Co-SiC with different particles loading in cobalt bath



Figure 5-24 Normalised metal thickness deposited per cycle against SiC vol. % for deposits with different SiC loadings compared to Co-WS₂ from an earlier work by Weston, et al [16]

Cathode current efficiency was calculated for all the produced coatings using the coatings thickness as follows, assuming that only Co and SiC particles were deposits:

$$th_i = V_i / A_{sub} \tag{5.1}$$

$$V_i = m_{dep} * w_i / p_i \tag{5.2}$$

$$th_i = \frac{V_{Co} + V_{particles}}{A_{sub}}$$
(5.3)

$$m_{dep:thickness} = A_{sub} * th * \left(\frac{w_{Co}}{p_{Co}} + \frac{w_{sic}}{p_{sic}}\right)^{-1}$$
(5.4)

where: th_i : Coating thickness, V_i : Volume of the component, A_{sub} : cross section area of the coating, m_{dep} : coatings mass, w_i :mass fraction, p: density.

Cathode current efficiency was calculated using Faraday law for the theoretical mass, where the deposited rate can be calculated from the following equation [129] considering the dissolved Co in the anodic pulse as following:

$$\eta = \frac{m_{Co:dep}}{m_{Co:th}} \tag{5.5}$$

$$m_{Co:dep} = m_{Co:dep:theor} - m_{Co:dis:theor}$$
(5.6)

Cathode efficiency for all the PRP coatings are in the range of 56-72%, Figure 5.25.



Figure 5-25: Cathodic efficiency of coatings with different particle loadings for different cathodic times with the consideration of the dissolution of Co.

5.3.2 Effect of SiC volume fraction on crystallite size reduction

Effect of the particle inclusion on grain size

Grain size measurements by XRD indicates that the grain size of cobalt matrix are in the range 50- 100 nm for all coatings. Grain size of coatings from 5 g l⁻¹ SiC particle loading bath and t_c = 60 s is 55- 62 nm. TEM analysis confirms that finding where the measured grains 50 - 100 nm, which means that XRD with EVA software can be used to estimate the grain size of Co. Cobalt grain size relation with the nano SiC particle vol. % can be presented clearly by plotting vol. % against grain size in both directions for coatings from each bath separately and correlating the relation between them, **Figure. 5.26**. The grain size values presented considered a range of SiC volume fraction from 1.8 % to 9.1 %. For Co-SiC with 5 g l⁻¹ SiC the grain size refinement can be seen clearly and is attributed to the nanoparticle inclusion mainly as no noticeable effect can be seen for the PRP in refining the grain size of the pure cobalt. The refinement can be explained because the grain size is mainly determined by the nucleation rate and the grain growth rate. According to the theory of electrodeposition, it has been suggested that the faster the nucleation rate, the slower the grain growth rate and the smaller the grain size [130]. When SiC nanoparticles are added to the plating bath solution, the nanoparticles

adsorbed onto the working electrode surface during the anodic phase and provide a large number of nucleation sites for the deposition process in case they were conductive. Moreover, these particles, distributed at the grain boundaries of the cobalt metal, impede the growth of grains, thereby reducing the grain size. This effect is also seen for the nanocomposites with particles loading up to 15 g l⁻¹ SiC, while no noticeable change in grain size for the other nanocomposites from bath with 20 g l⁻¹ SiC. These results combined with the SEM observation of the particle dispersion in high magnification **Figure. 5.26**, suggest that only good dispersion achieved 5-15 g l⁻¹ SiC loading with no agglomeration. Hence, coatings in this range will be considered to study their mechanical properties and model the governing strengthening.

5.4 Conclusion

- 1. PRP is better than DC in achieving higher particles inclusion.
- 2. Cross-sections of coatings and topographic characterizations demonstrated excellent adhesion to the mild steel substrate even for low duty cycles. This was obtained by applying a strike at the start of the electroplating.
- 3. Uniform particle dispersion was achieved with 5 g l^{-1} SiC as confirmed by EDX and TEM analysis. Some agglomeration with increasing SiC nanoparticle loadings at 20 g l^{-1} was observed for different t_c .
- 4. A maximum particle content was reached at 9.1 vol. % at 20 g l⁻¹. This particle content is considered as the saturation state as increasing the number of particles does not increase the particle included further.
- 5. The production of a well-dispersed nanocomposite Co-SiC using PRP and SDS technique is applicable for Co-SiC with particle loading up to 15 g l⁻¹ SiC. Hence, coatings in this range will be considered to study their mechanical properties and model the governing strengthening mechanisms.
- 6. Grain size measurements by XRD indicates that the grain size of the cobalt matrices are in the range 50- 100 nm for all coatings. Grain size of coatings from 5 g l⁻¹ SiC particle loading bath and $t_c = 60$ s is 55-62 nm. TEM analysis confirms that finding, where the measured grains 50-100 nm. This means that XRD with EVA software can be used to estimate the grain size of Co.

CHAPTER FIVE: MICROSTRUCTURAL CHARACTERISATION OF Co-SiC

7. It is suggested that a good dispersion is only achieved for 5-15 g l⁻¹ SiC loading avoiding agglomeration.



Figure 5-26: A plot of Co-SiC electrodeposits grain size against volume fraction of the SiC dispersed in the nanocomposites with different particle loadings in the range of 5 - $20 \text{ g} \text{ l}^{-1} \text{ SiC}$ and size 50 nm.

CHAPTER 6: Novel Co-Al₂O₃ Electrodeposited nanocomposites

6.1 Introduction

A review of data in the literature indicates that limited work on the co-deposition of ceramic particles with electrolytic cobalt has been conducted [131], as highlighted previously in chapter two. These nanocomposites include carbide nanoparticles: such as Cr_3C_2 [132], a few oxides Cr_2O_3 [133], ZrO_2 [134] and TiO_2 [135].

In this chapter, the co-deposition of nanocomposite cobalt matrix (Co-Al₂O₃) will be considered. These electroplated nanocomposites have not been covered before in the literature. The alumina particles used are 45 nm in diameter. Alumina nanoparticles were chosen for their strengthening effect due to their high hardness and wear resistance properties [7, 136]. The production of the selected nanocomposites will also allow further understanding of the applicability of the new PRP and anionic surfactant technique for different particles. In Chapter, 2 it was highlighted that many parameters play an important role in enhancing the incorporation of the nanoparticles into a metal matrix. In this work, the co-electrodeposition of the nanocomposites by PRP with ultrasound agitation will concentrate on the effect of only two different parameters: the time period of the cathodic pulse t_c, similarly like Co-WS₂ [16] and Co-SiC [78], and the anionic surfactant content. The cathodic time was varied in the following ranges: $t_c = 30$ s, 40 s, 60 s, 90 s, and 120 s, corresponding to duty cycles in the range of 43% to 86 %. The electroplated nanocomposites will also be compared to the conventional DC plating method coatings and to the coatings produced by PRP only (no surfactant). Five different concentrations of SDS ranging from 0.0 to 0.8 g l⁻¹ were investigated, taking into account the drawback of using a high concentration of SDS found in a preliminary work in the Co system where particle incorporation rose to a maximum with increasing SDS content and thereafter decreased [78].

6.2 Results

6.2.1 Field Emission Gun Scanning Electron Microscopy FEGSEM Characterization

I. Cross section

Firstly, the effect of the PRP only for the Co-Al₂O₃ coatings produced with 0.0 g l⁻¹ SDS and different duty cycle were investigated. BSE cross-section images are shown in **Figure 6.1**. They show that all the coatings with t_c = 30 s -120 s and DC have a good adhesion to the substrate, which attributed to the applied DC strike prior to the PRP electroplating. Some voids at the interface between the coatings and the substrate can be seen with low duty cycle accompanied by some extended voids through coatings cross section from low duty cycle, **Figure 6.1**, **i**, corresponding to the coating at t_c = 30 s and 0.0 g l⁻¹ SDS.



Figure 6-1: FEG-SEM cross-section images of coatings from bath 3a-PRP with different t_c: i) 30s with highlighted dissolution at the interface area between the coating and the substrate as well as some extended microcracks to the coating , ii) 60s, iii) 90s, iv) DC

Cross section images of the coatings with 0.0 g 1^{-1} content with high magnifications, **Figure 6.2** showed that alumina particles are dispersed through all the coatings from bath B-3a with 0 g 1^{-1} SDS surfactant, but with different content. The included particles decrease with increasing duty cycle up to $t_c = 120$ s, where much lower particle content can be seen clearly, **Figure 6.2** iv, and v. Coatings produced by DC showed agglomerated particles through the coating, **Figure 6.2** vi. Podlaha produced nanocomposite Cu-Al₂O₃ by PRP with no surfactant and suggested that results in higher particle inclusion compared to the DC due to the metal dissolution in the anodic pulse resulting in eliminating the metal concentration and increase the particle content. In the current study the higher particle content of the produced Co-Al₂O₃ with 0.0 g 1^{-1} SDS with the lower tc can be explained by the higher amount of the dissolved metal compared to the incorporated particles resulted in higher particle content in the coating.

Coatings produced with the addition of SDS showed similar effect of duty cycle, where voids at the interface between the substrate and the coating resulted with coatings produced with low duty cycle. A representative coatings from bath B3-b with 0.2 g 1^{-1} cross section showed not big change in appearance of the particle content compared to the coatings produced with 0.0 g 1^{-1} SDS, **Figure, 6.3 i, iii, v**. However, all the cross section of coatings from B3-a with no SDS showed rough surface compared to the coatings of B3-b with 0.2 g 1^{-1} SDS, **Figure 6.3 ii, iv, vi**. Surface roughness could be related to the effect caused by the particle inclusion.





Figure 6-2: BSE image of Co-Al₂O₃ from bath 3-a with 0.0 g l⁻¹ SDS, presenting particles dispersion through the cross-sections for different t_c: i) 30 s, ii) 40 s, iii) 60 s, iv) 90 s, v) 120 s, vi) DC





Figure 6-3: BSE image of Co-Al₂O₃ from bath 3-a, and b (with 0 g l⁻¹ SDS and 0.2 gl⁻¹ SDS) with t_c: i) 30 s, ii) 60 s, iii) 90 s and 0.2 g l⁻¹ SDS and t_c = iv) 30 s, v) 60 s vi) 90 s respectively.

The effect of surfactant concentration was investigated by producing coatings from baths with different SDS concentration in the range 0.2 - 0.8 g l⁻¹. Cross-sections images demonstrate the rising appearance of micro cracks with higher SDS up to 0.8 g l⁻¹ for different duty cycle. **Figure 6.4, i-iv** revealed that for selected specimens of $t_c = 60$ s. Electroplated deposits with 0.6, and 0.8 SDS g l⁻¹ SDS showed non-adhesive, cracked, and brittle cross sections, while deposits without surfactant showed no cracks. This could be the result of the adsorption of the SDS to the plating surface resulting in stressed and brittle surface as was reported in a former work [28, 34]. Hence, this restricts the use of SDS percent to below 0.6 g l⁻¹ for the electrodeposition of Co-Al₂O₃. Coatings thickness was shown to be increased with increasing the duty cycle for all coatings from different SDS concentration in the bath, **Table 6.1**, and can be seen more clearly in **Figure 6.5**.



Figure 6-4: FEGSEM cross-section images of coatings from bath 3-PRP with tc= 60 s with the effect of SDS addition: i) 0.2 g l⁻¹, ii) 0.4 g l⁻¹, iii) 0.6 g l⁻¹, iv) 0.8 g l⁻¹

Doth		Coatings thickness - μm								
Daui	tc-s	30	40	60	90	120	DC			
3 a		24.5	26.2	31.5	31.9	31.8	36.6			
3 b		24.5	27.8	32.0	37.0	39.0	31.8			
3 c		27.7	26.9	30.7	36.2	36.5	38.9			
3d		29.1	30.1	34.1	33.4	36.4	35.9			
3 e		24.9	28.0	24.1	32.0	38.5	36.6			

Table 6-1: Average thickness calculated from FEGSEM images



Figure 6-5: Co-Al₂O₃ coatings cross section thickness against the cathodic time for the different SDS content

II. Surface topography

The surface topography of representative coatings is shown in **Figure 6.6**. The coatings surface revealed needle-like cobalt grains with a selective dissolution on the surface of the PRP coatings, **Figure 6.6**, **i-iii**.

Cobalt particles are oriented at different directions parallel to the substrate as can be seen in all the selected images of the coatings of PRP and DC. The size of the matrix cobalt particles varied for each coating but not in a big difference for the PRP coatings with altered t_c. Also, the cobalt particle size is smaller for the coatings produced by PRP compared with DC coatings, **Figure.6.6**, **iv**. This is accompanied by random voids especially with low duty cycles coatings 30 s and 40 s that could be extended from the microcracks at the interface of the substrate with the films observed in cross-section up to 50 μ m². **Figure 6.6**, **iv** shows the surface of DC coatings with no seen porosity as for the PRP. Alumina particles cannot be seen clearly from the surface of the coatings of PRP coatings, while random particles can be seen on the topography of DC coatings.



Figure 6-6: Topography FEGSEM of: i) 3b-30 s with spread voids through the coatings surface, ii) 3-b-60 s cobalt matric particles with alumina particles imbedded, iii) No big change in Co matrix grain size with t_c= 90 s, iv) 3b- DC

6.2.2 Energy disperse X-Ray EDX Analysis

EDX analysis has been performed to analyse the chemical composition of the coatings: nano particles content, effect of PRP on oxygen content and particle distribution through the coatings, as well as any other elements or compound that may form on the coatings surface.

The analysis performed at five positions across each coating with an accelerating voltage of 20 kV for bath 3 - coatings. The analysis showed the presence of aluminium, cobalt and oxygen in all coatings. Rare traces of low iron concentrations were dismissed as the

iron peak overlaps with the cobalt peak in the EDX spectrum. From bath 3- coatings with alumina particles, spectra were acquired for the elements Al and Co. Additional spectra were obtained to respect traces of oxygen. All the raw data of the measurements are presented in **Appendix 2** for the averaged results in combination with the standard error deviation SSD for Co-Al₂O₃.

In order to investigate the effect of PRP with different duty cycle, and the effect of PRP with different SDS on the content of the particle inclusion and the particle distribution, the volume fractions will be calculated for all the coatings.

From the atomic ratios, the particle volume fractions were calculated twice: Once neglecting the oxygen given by EDX analysis and the other time assuming that all free oxygen was present as Co (OH)₂ molecules. For alumina including Co (OH)₂, the calculation is as follows: The number of free oxygen atoms is equal to the number of oxygen present minus the amount of aluminium atoms times 1.5 because alumina has the chemical formula Al₂O₃. Since Co (OH)₂ molecules contain the same amount of hydrogen as oxygen, hydrogen which cannot be detected by EDX, is assumed to be present in the same quantity.

$$n_0, free = n_H = \max(0, n_0 - 1.5, n_{Al})$$
 (6.1)

The mass of a component m and the mass fraction W_i are calculated by regarding the amount of atoms present in the molecule:

$$m_{Al_2O_3} = n_{Al} (M_{Al} + 1.5, M_0)$$
(6.2)

$$m_{Co}(OH)_2 = n_{H} (M_0 + M_H + \frac{M_{Co}}{2})$$
(6.3)

$$m_{Co} = (n_{Co} - \frac{n_H}{2}). M_{Co}$$
 (6.4)

$$W_i = \frac{\sum m_i}{m_i} \tag{6.5}$$

By applying the density ρ_i the volume V and volume fraction υ can be calculated:

$$V_i = m_i / \rho_i \tag{6.6}$$

where: M_i molecular weight of an element, V_i : Volume of the component, m_{dep} : coatings mass, w_i :mass fraction, p : density.

The results of the calculations are presented in **Table 6.2**. The calculations indicated the availability of oxygen in high content in the coatings, which is assumed to be available as $Co(OH)_2$, up to 18%. These values were dismissed as the oxygen was not detected in the cross section of the coatings in FEGSEM analysis.

		Excl	luding	Including Co(OH)2				
Bath	t _c	Al ₂ O ₃	Co(OH) ₂	Co(OH) ₂				
	[s]	[wt.%]	[vol.%]	[wt.%]	[vol.%]	[wt.%]	[vol.%]	
	30	2.9	6.3	2.4	5.1	3.0	6.9	
	40	2.6	5.7	2.6	5.5	2.9	6.6	
	60	1.6	3.5	1.5	3.2	2.4	5.7	
	90	2.2	4.7	2.1	4.4	1.9	4.5	
3a	120	2.2	4.8	2.2	4.6	2.2	5.1	
	DC	2.4	5.3	2.3	4.8	3.5	7.9	
	30	3.2	6.9	3.0	6.1	3.6	8.1	
	40	3.4	7.2	3.3	6.7	4.0	8.9	
	60	2.5	5.4	2.4	5.0	3.1	7.2	
	90	2.7	5.9	2.5	5.1	3.3	7.6	
3b	120	3.0	6.4	2.8	5.7	4.7	10.5	
	DC	2.6	5.6	2.4	4.9	4.0	9.1	
	30	4.3	9.2	3.5	6.7	8.5	18.0	
	40	3.6	7.7	3.4	6.6	7.1	15.3	
	60	2.8	6.1	2.3	4.6	5.1	11.5	
	90	2.9	6.3	2.3	4.8	3.7	8.4	
3c	120	2.6	5.6	2.4	5.0	4.4	9.9	
	DC	2.4	5.3	2.3	4.8	3.1	7.2	
	30	3.7	8.0	3.2	6.4	5.2	11.5	
	40	3.8	8.1	3.4	6.7	4.9	10.9	
	60	3.2	6.8	2.8	5.8	3.9	8.8	
	90	2.7	5.9	2.5	5.2	4.4	9.9	
3d	120	2.4	5.2	2.2	4.6	3.9	8.9	
	DC	2.6	5.5	2.4	4.8	4.0	9.2	
	30	3.3	7.1	3.1	6.1	5.3	11.8	
	40	3.8	8.2	3.5	7.0	4.8	10.7	
	60	3.2	7.0	2.9	5.9	5.2	11.6	
	90	2.4	5.2	2.2	4.5	3.6	8.1	
3e	120	2.6	5.6	2.4	5.0	3.9	8.9	
	DC	2.4	5.2	2.1	4.3	4.3	9.8	

Table 6-2: Calculated Vol. % of the Co-Al₂O₃ coatings with and without oxygen

The EDX results are presented in **Table 6.2** and are shown in plots **Figure 6.7** and **Figure 6.8**. The first figure (**Figure 6.7**) shows coatings from bath B3-a produced by DC with particle vol. % up to 4.9. **Figure 6.8** shows coatings from the same bath and produced by PRP. A slight increment in particle content with decreasing tc can be seen clearly. The vol. % of the nanoparticles reaches 5.1- 5.5 vol. % at tc= 30 s and 40 s respectively, **Figure 6.8**.

Coatings produced with 0.2 g l⁻¹ and DC showed similar particle content to the coatings from the previous bath with 0.0 g l⁻¹ 4.9 vol. %. PRP coatings showed increased particle content compared to the PRP coatings from 0.0 g l⁻¹ SDS. The highest particles vol. % achieved with t_c = 30 s, and 40 s 6.1-6.7 vol. %, **Figure 6.7** and **Figure 6.8**. The Al₂O₃ particle content from this bath is lower compared to the particle content of Co-WS₂ of 13-18 vol. % and Co-SiC 10-13 vol. % produced from the same bath composition and with t_c =30 s – 40 s respectively in previous works on Co - WS₂ and Co - SiC by Weston et al [16]. This change in particle content was reported [18] to be caused by the change in crystal structure as proved in previous work on SiC [110] and Al₂O₃ [34, 136].

Further increment in SDS content 0.4 g l⁻¹ SDS in coatings produced by DC resulted also in similar vol. % as for 0- 0.2 g l⁻¹ SDS 5.3 vol. %. On the other hand, coatings from different PRP resulted in an additional enhancement in particle content up to 9.1 vol.% at $t_c=30$ s which is the peak of the particle inclusion. Beyond 0.4 g l⁻¹ SDS the highest particle content reached 8.1- 8.3 which is approximately similar to the o.4 g l⁻¹ effect. Particle inclusion increment with increasing SDS can be attributed to the effect of the absorbed SDS on the particle surface and giving them a negative surface charge, which results in repealing the particles of the same charge each other and became more stable in the electrolyte without agglomeration. The promoted surface charge will increase the affinity of the particle to the cathode at the anodic pulse and hence increase the particle inclusion to the cathode.



Figure 6-7: Alumina vol. % in Co-Al₂O₃ against SDS concentration of Co-Al₂O₃ produced by DC



Figure 6-8: Volume fraction of Al₂O₃ against cathodic time t_c for coatings from bath 3a-e with different SDS concentration

The effect of the SDS concentration on the particle inclusion was highlighted by plotting the alumina vol. % against SDS content in **Figure 6.9**. The plot shows that the maximum vol. % achieved at SDS= 0.4 g l⁻¹, where no further increment in the particle inclusion was obtained. This could be attributed to the formation of the micelle by the surfactant. At high SDS concentration, the SDS will forms micelle in the bath and tend to react together. They disrupted the particle inclusion and leading to a decrease in their incorporation. Therefore, an optimum concentration that can achieve the highest particle inclusion which is $0.4 \text{ g } l^{-1}$ for this system Co-Al₂O₃. Beyond that the dispersion quality and number of the incorporated particles will decrease and the free surfactant will increase and will be adsorbed into the coatings resulting in coatings brittleness [28, 44].



Figure 6-9: EDX analysis represented by volume fraction of Al₂O₃ nanoparticles with different SDS surfactant content.

6.2.3 Image analysis

It's been shown that coatings with low duty cycle contain voids at the interface between the coatings and the substrate. Image analysis was used to measure the voids fraction of a representative area of the cross section from FEGSEM images with low magnification

of all the coatings, **Figure 6.10**. The measured voids fractions are given in **Table 6.3** and showed that there are some voids at low t_c and disappeared at higher tc than 40s.

Bath	30 s	40 s	60 s	90 s	120 s	DC
3 a	0.8	0.9	0	0	0	0
3b	0.5	0.3	0	0	0	0
3c	0.8	0.7	0	0	0	0
3d	1.5	0.5	0	0	0	0
3e	0.8	0.9	0.9	0.1	0	0

 Table 6-3:
 Void % sub-coat from image analysis



Figure 6-10: the voids formed in coating and substrate

6.2.4 Deposited Mass

Experimentally, the mass was calculated before and after the plating, considering the amount of the dissolved zinc from the substrate during the surface preparation. This was

done by measuring the amount of the dissolved zinc for four specimen substrates, and the average mass dissolved zinc was 10.33 mg that was taken from all mass measurements. The voids that formed at the steel– coating interface were considered to find the dissolved part of steel at the beginning of electroplating on the anodic pulse. The measured deposited mass are presented in **appendix 3**.

From the measured mass, the theoretical thickness of the coating was calculated for all layers as follows:

$$th_i = V_i / A_{sub} \tag{6.7}$$

$$V_i = m_{dep} * w_i \tag{6.8}$$

And considering the voids through the coatings to calculate the volume gives:

$$th_{th} = th_{Co} + th_{particle} + th_{voids}$$
(6.9)

$$\frac{V_{Co} + V_{particles} + V_{voids}}{A_{sub}}$$
(6.10)

$$V_{voids} = V_{sub} * v_{void \ coat} \tag{6.11}$$

$$A_{sub} * t * v_{voids \ coat} \tag{6.12}$$

$$th_{th} = \frac{m_{dep}}{A_{sub}} \cdot \left(\frac{w_{Co}}{\rho_{Co}} + \frac{w_{particles}}{\rho_{particles}}\right) \cdot \left(1 - v_{voids\ coat}\right)^{-1}$$
(6.13)

 th_i : Coating thickness, V_i : Volume of the component, A_{sub} : cross section area of the coating, m_{dep} : coatings mass, w_i , ρ : density, $v_{voids \ coat}$: the measured void fraction of the coating. The calculated thickness for all the coatings are presented in **Table 6.4**. Coatings thickness increases with increasing duty cycle for the all coatings from bath B3a-e.

Bath	tc(s)	30	40	60	90	120	DC
3 a		27.1	32.3	37.8	44.3	47.7	48.2
3b		23.2	31.3	38.4	42.7	47.7	48.9
3 c		24.5	32.9	39.2	44.6	46.9	48.5
3d		28.7	31.4	38.8	44.2	46.1	48.4
3 e		23.8	34.7	38.4	45.8	46.8	47.9

Table 6-4: Coatings thickness calculated from the deposited mass

6.2.5 Cathodic Efficiency

Assuming only Co and Al_2O_3 particles are dispersed into the matrix, and using the measured coating thickness and duty cycle the cathodic current efficiency for all coatings from bath 3 was calculated. The calculations performed in a similar way to the calculation in chapter 5, and presented in Appendix 3,

Also, the cathode efficiency was calculated using the experimental measured deposited mass, using **Equation 6.13 and is** given in **Appendix 4**.

Cathode current efficiency η was calculated using Faraday law for both theoretical mass and experimental one, where the deposited rate can be calculated from the following equations:

$$\eta = \frac{m_{Co:dep}}{m_{Co:th}} \tag{6.14}$$

$$m_{Co:dep} = m_{Co:dep:theor} - m_{Co:dis:theor}$$
(6.15)

Cathode efficiency calculated from both procedures followed the same trend, and presented in **Figure 6.11**, and **Figure 6.12**. **Figure 6.11** shows that the cathode efficiency of the cobalt coatings calculated from the coatings thickness is in the range of (90 % - 98 %). **Figure 6.12** shows that the cathode efficiency calculated from the deposited mass is

in the range of (76% - 88%). The difference in the cathode efficiency calculated from both procedures is related to the difference in mass deposited value. The mass deposited measured value does not take into consideration the formed voids as well as there might be some error in the measurements resulted from the removed zinc after etching the surface. While these two source of errors are not available in the measurement of the deposited mass from the measured thickness. Hence, the cathode efficiency calculated from the measured thickness would be more reasonable. Nevertheless, both plots show lower duty cycle have the highest efficiency compared to the coatings produced from higher duty cycle and DC. This behaviour could be explained due to the increase of Co^{2+} concentration in the near WE region during the anodic dissolution phase with the lower duty cycle [16]. The Co^{2+} is decreased down to steady state levels at $t_c= 90$ s. Cathode efficiency of the cobalt in this study is much higher than the cathode efficiency for the chrome plating that reaches at best around 20% as reported in literature.



Figure 6-11: Cathode current efficiency of Co-Al₂O₃ calculated from the measured thickness against cathodic time t_c



Figure 6-12: Cathode current efficiency of Co-Al₂O₃ calculated from the measured mass against cathodic time t_c
Plotting the cathode efficiency against the SDS content to investigate the effect of the surfactant on the cathode efficiency, **Figure 6.13** revealed that there is no decrement in cathode efficiency with the different SDS concentration, which indicates that the SDS addition is not impeding the Co deposition as the metal deposition occur in the cathodic pulse and separated from the controlled particle incorporation. This effect can be clarified by comparing the cathode efficiency for the metal matrix with the availability of a cationic surfactant. Rudnik et al [69] investigated the effect of the CTAB on the incorporation of nano SiC into Ni matrix and using DC. She suggested that increasing the cathode particle on the CTAB surface that will be available close to the cathode and results in decreasing the Ni²⁺ ions deposited on the cathode. This can be explained due to the competitive deposition of the metal and the particles incorporation at the same time. This behaviour was also proved in an earlier study by Weston et al [16].



Figure 6-13: Cathode current efficiency of Co-Al₂O₃ against SDS concentration

6.2.6 X-Ray Diffraction Analysis

XRD patterns for all Co-Al₂O₃ nanocomposites coating showed only hcp cobalt peaks at (100) and (110). No oxygen peak was recognized throughout all the coatings patterns.

The XRD patterns for different duty cycles showed that increasing the duty cycle results in an increase in the Co (100) peak intensity and a decrease in the (110) peak for both sets of coatings. By defining the position of the alumina peaks from the analysed pure powders of Al_2O_3 the resulted patterns from all the coatings showed no noticeable peak for the alumina. **Figure 6.14**, showed the XRD pattern for a selected bath B3-b with 0.2 g l⁻¹ SDS and different duty cycle.

The XRD patterns of the nanocomposites for different soap concentrations, for a 0.71 duty cycle, are displayed for Co-Al₂O₃ in **Figures 6.15**. The patterns show two representative peaks for cobalt as for the previously produced coatings in this work. The patterns show a reduction of the Co peaks intensity for the direction (100) and increase in peak intensity in (110) direction with increasing SDS content, as for the DC films. This behaviour can be seen clearly for all the coatings up to 0.4 g l^{-1} SDS.

Also, the Co peaks in **Figure 6.15** broaden with the higher SDS, which indicates a variation in crystallite size. The crystallite size was calculated by importing the reference sample file and the experimental XRD pattern for the selected batch of the coatings k α 2 was removed firstly (stripped). The instrumental broadening was found by working out the nearest peak of the cobalt (100) or (110) and the imported corundum reference, and using **Equation 4.10** assuming that the peak shape is Cauchy. Then crystallite size was found using the Scherer equation using EVA software.



Figure 6-14: XRD pattern for Co-Al₂O₃, from B3-b and different cathodic time t_c



Figure 6-15: XRD pattern for Co-Al₂O₃, $t_c = 60$ s with different SDS concentrations

Tuble of el filst unionital mile of outering, futues obtained after stripping 1142						
Co peak [° 20]	Si peak used [° 20]	Instrumental line broadening				
		[°]				
41.49 (100)	41.8 (220)	0.102				
75.83 (110)	76.4 (331)	0.114				

Table 6-5: Instrumental line broadening, values obtained after stripping Ka2

Grain size plotted against the Al₂O₃ vol. % for all the coatings in both directions 100 and 110, **Figure 6.16** and **Figure 6.17**. The calculated grain size from both directions showed a refinement with increasing particles vol. % up to 9% with grain size in the range (60 - 120) nm in 100 direction and (60 - 140) nm in 110 direction. The grain size of cobalt from baths with different SDS is higher than the grain size refinement of the Co-SiC produced from different particle loading 5- 20 g l⁻¹ SiC in the previous chapter with vol. % up to 9. This can be attributed to the agglomeration of the nanoparticle with only 0.2 g l⁻¹ SDS compared to the range of the SDS content for the Co-Al₂O₃.



Figure 6-16: Grain size distribution of cobalt matrix in 100 with different Al₂O₃ particles vol.%



Figure 6-17: Grain size distribution of cobalt matrix in110 with different Al₂O₃ particles vol.%

6.3 Discussion

6.3.1 PRP and SDS mechanism

All coatings showed good bonding to the substrate that was attributed to the DC strike applied before to PRP electrodeposition in a similar way to the coatings of Co-SiC in the previous chapter.

Coatings of bath B-3a with no SDS with different t_c showed distributed particles through the thickness of the coating with no promoted particle content with different t_c. The particle content for these coatings was lower than that produced from baths 3b-e. This behaviour was accompanied by lower cathodic efficiency with different tc, **Figure 6.12** SDS anionic surfactant addition resulted in higher alumina nanoparticle content of the nanocomposite up to a maximum at 0.4 g l⁻¹, compared to a maximum content achieved at 0.6 g l⁻¹ SDS for Co-SiC electroplated nanocomposite produced in an earlier work [78]. This is accompanied by increasing the particle content with decreasing duty cycle for each SDS content, similarly to the results of the Co-SiC in the previous chapter and the previous work [78] on Co-SiC.

Additionally, coatings produced from bath B3 by DC showed dispersed alumina particles throughout the cross-section of the layers with no significant change in particle inclusion

with increasing SDS content. This could be attributed to the absence of the electrophoretic effect on alumina particles resulted in a random arrival, adsorption and encapsulation of particles into the cobalt following the Guglielmi model. The first step in this model, the particle approaching the cathode become loosely adsorbed on the cathode surface. The loosely adsorbed particles are still surrounded by a cloud of adsorbed cobalt ions. Then in the second step, the particles loose the ionic cloud and become strongly adsorbed on the cathode. The results showed similar particle contents for all DC coatings with and without SDS, **Figure 6.7**.

EDX analysis showed the availability of oxygen throughout all the coatings produced by DC and PRP in different value up to 18%. However, both the cross section analysis in FEGSEM and XRD did not show the oxygen that should be seen. Hence, the results were not considered.

For comparison with these earlier studies, **Figure 6.18** and **Figure 6.19** plots present the deposited thickness per cycle, which is measured by FEGSEM, normalized by the particles diameter against the particle volume fraction for all the electroplated layers produced from different tc and for the previous work. It can be seen that the nanocomposites $Co-Al_2O_3$ is behaved differently compared to the $Co-WS_2$ nanocomposites. This could be attributed to the particles characteristic from both system that affect their inclusion. The $Co-Al_2O_3$ nanocomposites produced with various SDS are shown in **Figure 6.18**. The particle volume fraction reaches 9% at the lowest normalised coating thickness per cycle, as in the previous work on PRP by [16] and [7]. **Figure 6.20** illustrates the rise in particle volume fraction as the deposited Co thickness per cycle reduces, reaches the maximum value at short deposited cobalt layer with short t_c for most of the films.



Figure 6-18: Volume fraction of the alumina nanoparticles plotted against the normalised deposited cobalt thickness to the particle diameter per cycle for different SDS content and tc



Figure 6-19: Volume fraction of the alumina nanoparticles plotted against the normalised deposited cobalt thickness to the particle diameter per cycle in this study compared to the previous study by Weston [16] for 0.2 g l⁻¹ SDS and different t_c.

It's been mentioned that the number of particles encapsulated in each cycle can provide more information about the mechanism of the particle arrival to the cathode [16, 119]. To calculate the number of the particles per each cycle. Firstly, it would be suitable to subtract the particles that arrive randomly due to the effect of the mechanical entrapments in DC. Then, calculate the number of the particles captured, which is encapsulated by the PRP/SDS effect. The calculated particles number is plotted versus the metal thickness deposited per cycle normalised to the particle diameter, **Figure 6.20**. The plot showed that for 0 g l⁻¹ SDS content the particle capture is not following the same pattern for the particles captured with SDS addition (0.2 - 0.8) g l⁻¹ SDS. Also, the plot shows that at low SDS the particle incorporation is high. These results are comparable to the behaviour of the other produced nanocomposite electroplated coatings Co-SiC, **Figure 6.21**.

The plot demonstrates that PRP can bring more particle than particles brought by DC plating. The number of the particles brought in exceed close packing on a flat plane therefore the particles do not form a neat single layer and extra particles are captured out to a coating thickness, which is dictated by SDS layer. This can be interpreted as increasing the nanoparticles concentration in the near working electrode (WE) region during the anodic pulse. For 0.0 g l⁻¹ SDS, it can be seen that there must be a significant negative charge on the Al₂O₃ particles, as there is a small spike and then a levelling off. Adding 0.2 g l⁻¹ and more particles are captured at 30s and 40s, but thereafter the additional effect is much less at 0.4 g l⁻¹ SDS more captured but similar, at 0.6 g l⁻¹ SDS the effect is much greater and similar at 0.8 g l⁻¹. Keeping in mind that the DC contribution has particles arriving and being captured all the time. Al₂O₃ is much better at this than SiC, so there will be an equivalent baseline of particles representing a fractional coverage and these are in addition to the ones here.



Figure 6-20: Surface coverage of alumina particle fraction per cycle against the cobalt deposited per cycle in PRP with different SDS concentration in the bath



Figure 6-21: Surface coverage of SiC nanoparticles fraction per cycle

6.3.2 Effect of particle volume fraction on crystallite size

The calculated crystallite size presented in **Figure 6.17** Plotted again in the two (100) and (110) to calculate the variation of the grain size with texture. A plot of Al₂O₃ volume fraction and cobalt grain size is also is presented in Figure 6.22 to look for any relationship for this nanocomposites in a similar way to that presented in chapter five for Co-SiC. The plot represents the relationship between crystallite size and volume fraction, with data presented separately for each SDS content to find the dispersion effect of each bath. The plots confirm that crystallite size decreases with increasing volume fraction of nanoparticles in a similar trend for all the coatings in both (100) and (110) peaks. The Co grain size decreases noticeably with increasing volume fraction for most of the coatings. Crystallite sizes from the (110) plane show approximately the same pattern of behaviour compared to the (100) planes. The grain size decrement is clear for the coatings from each SDS content, with grain size in the range of 60-120 nm in similar way for each SDS content. It can conclude that the grain size of Co-Al₂O₃ is in the same range of Co-SiC that was 50-100 nm. The seen decrement is contributed either to the particles inclusion or due to the effect of the PRP. As the pure cobalt produced by PRP and different t_c demonstrated an approximate similar grain size then it can be assumed that the refining was resulted by the nanoparticles inclusion in the cobalt matrix.



Figure 6-22: Co-Al₂O₃ grain size against volume fraction of particles for different SDS contents

6.4 Conclusion

For the first time, alumina (Al₂O₃) nanoparticles co-electrodeposited in cobalt using pulse reverse plating (PRP) and an anionic surfactant to achieve increased particle deposition and dispersion. Conventional direct current (DC) electrodeposition also undertook for comparison. The influence of various concentrations of the anionic surfactant sodium dodecyl sulphate (SDS) from a range of 0.0 to 0.8 g l^{-1} in the bath, as well as different

duty cycles from 43% to 100%, investigated. Furthermore, crystallography of the composite coatings assessed by FEGSEM, sectioning and topography, energy dispersive X-ray analyser (EDX), image analysis, and X-ray powder diffraction (XRD). Results from this study suggest that the highest volume fraction of alumina nanoparticles can be obtained with a duty cycle of 57% and 71% for alumina nanoparticles. FEGSEM analysis showed that duty cycles below 57% led to a high void fraction in the coating due to anodic dissolution. A concentration of the anodic surfactant above 0.2 g l⁻¹ in the bath led to widespread brittleness, which might be resulted due to the effect of the bath chemistry as highlighted previously [67]. Hence, more XPS analysis is required for surface of the coatings with different SDS.

EDX analysis indicated the existence of cobalt (II) hydroxide but this was not supported by FEGSEM analysis or XRD. All coatings showed excellent adhesion to the substrate. Also, it's suggested to measure the surface roughness to understand the effect of the PRP with and without SDS.

Anodic dissolution at low duty cycles was observed and needs to be prevented in further studies. Both the t_c and SDS change the crystallite growth direction and size. Increasing vol. % resulted in reducing the grain size in both Co hcp structure directions with grain size in the range of 60 - 120 nm for particle vol. % of 0 - 9.

CHAPTER 7: PRODUCTION OF Co-PTFE COMPOSITES

7.1 Introduction

Co-electrodeposition of solid lubricant particles are well-known to enhance the tribological characteristic of metal matrix composites and have been extensively studied previously [20]. The produced electrodeposited composite may not only be used to prolong the machine durability by reducing wearing of the component but also to permit unlubricated sliding. This predestines these coatings for the use in aquatic environments where lubrication is impossible [137] and for the food or chemical industry where lubrication is restricted. One of the common used particle to enhance the lubricity of the metal matrix composite is the Polytetrafluoroethylene PTFE particle. PTFE used for tribological applications and high corrosion resistance composites materials [138] due to their lubrication influence, with a low coefficient of friction and anti-stick characteristics [138-140]. In addition to the previous characteristics, the superhydrophobicity characteristic of the PTFE particles allows them to be used combined with engineering materials for practical applications. These applications include self-cleaning, anti-icing, anti-fouling, anti-corrosion and reduced fluid drag surfaces.

Using the electrodeposition technique for the synthesis of the superhydrophobic surface holds a number of potential benefits over other techniques. This is due to the advantage of using electrodeposition of being both scalable and cost effective. The use of a nanocrystalline metal matrix will provide a coating with high strength additionally to superhydrophobicity resulting in a multifunctional coating. Also, the aim is that the co-deposition process permits a uniform dispersion of the hydrophobic particles throughout the coating thickness. This means that as the surface of the coating wears down during service, PTFE hydrophobic particles will be continually exposed to the surface allowing for the potential of a long lasting superhydrophobic surface [141].

The water-repellency characteristic of the PTFE particles makes them hard to disperse in aqueous solution without any modification onto their surfaces. Thus, it is of vital importance to consider this to achieve a good dispersion and suspension of these particles so as to co-deposit a sufficient number of particles and avoid the particle agglomeration in the plating bath. This characteristic was taken into consideration in literature and it was suggested to use a certain surface-active agent to the plating bath to overcome the low wettability of the particles [64, 139-141]. The dispersing function of surfactant arises from the adsorption of surfactant on the surface of PTFE particles. According to the

literature, it's suggested that good PTFE particle content of diameter less than 1µm can be achieved by using non-ionic surfactant, cationic surfactant and anionic surfactant [64, 139-142]. Also, it should be mentioned that most of the previous work concentrated on co-deposition of the PTFE into nickel matrix. No work has been found on the coelectrodeposition of the PTFE into cobalt matrix.

The intent of the present work is to study the behaviour of the Co -PTFE using 1 μ m PTFE particle size and using the proposed PRP technique and anionic surfactant. The purpose is to co-deposit two particles into cobalt matrix in the future: Al₂O₃ that possesses high hardness and wear resistance (that was successfully produced by PRP and anionic surfactant in chapter six), and the PTFE that known for its high lubricant properties, which will be produced in this chapter.

The electroplating parameters were selected with three different t_c : 30 s, 60 s, and DC, and SDS (0 - 0.8) g l⁻¹.

7.2 Results

7.2.1 Field emission gun scanning electron microscopy (FEGSEM) Characterization

I. Cross section

Cross sections of the Co-PTFE coatings from bath B4-a-e performed good adhesion to the substrate with voids formation for the coatings produced from $t_c = 30$ s due to the anodic dissolution at the beginning of the electroplating, similarly to the behaviour of the Co-Al₂O₃.

Coatings produced with no anionic surfactant showed no particle inclusion, which is expected due to the low wettability of the particles. SDS addition produced coatings with few particles, limited dispersion in occasional areas, **Figure 7.1**, **i**. The same behaviour was seen through the cross section of the different SDS content. High magnification images **Figure7.1**, **iii** demonstrate PTFE particle sizes of approximately 300 nm instead of the used 1µm particle diameter.

Coatings produced with different duty cycle and with similar SDS content showed also limited particles inclusion with particle size of about 300 nm. Coatings thickness were in the range of $31-38 \mu m$.



Figure 7-1: BSE images of bath 4 and 0.2 g l⁻¹ SDS for Co-PTFE cross section: i) t_c= 30 s, ii) t_c=60 s

II. Surface topography

The topographical analysis of the coatings top surface showed needle like of cobalt plated in different direction with some porosity that can be seen clearly particularly for coatings produced by PRP, as shown in **Figure 7.2 i**, **ii** for a coating of t_c = 60 s and DC respectively from bath B4-b. No PTFE particles can be seen through the coatings topography, **Figure 7.2**.



Figure 7-2: Topography of PRP and DC coatings from bath 4b with0.2gl⁻¹ SDS: i)t_c=60 s, and ii) DC

7.2.2 EDX analysis

EDX analysis of all the coatings produced from bath 4 showed the availability of Co and F spectra. F is overlap with the Co peak, **Figure 7.3** that shows the EDX analysis for a Co-PTFE coating from this work. The results of EDX for all the coatings are presented in **Table 7.1**, **Table 7.2** for at. % and calculated vol. % of the PTFE particles respectively. The results show high F at. % that reaches 6.2 for t_c = 60 s from B4-b. This is contrary to the result from the inspection of cross-sectional images, which was very much lower, and closer to 1% by volume. The overlap of the EDX peaks of cobalt and fluorine are expected to account for this discrepancy, **Figure 7.4**. For this reason, the image analysis was performed for coatings from bath 4.



(11)		
Element	Weight%	Atomic%
F K	2.08	6.18
Co L	97.92	93.82
Totals	100.00	



(iii)

Figure 7-3: EDX analysis of a selected coating of Co-PTFE showing the peak overlap of Co and F:i) The selected area for the analysis of the coating cross section with high magnification, ii) chemical composition of the elements, and iii) EDX spectra

Table 7-1: EDX analysis showing the chemical composition of coatings from bath 4 for Co-PTFE showing high particle content and no clear trend

Bath	F (at. %)	SSD	F (at. %)	SSD	F (at. %)	SSD
	30 s		60 s		DC	
4a	0	0	5.4	0.4	5.2	0.8
4b	5.3	0.9	6.3	0.5	6.2	0.3
4c	5.7	0.3	5.6	0.3	5.8	0.3
4d	5.1	0.9	5.9	0.7	6.1	0.3
4e	5.3	0.5	5.3	0.3	5.5	0.5

 Table 7-2: Calculated Vol. % of the Co-PTFE coatings shows high PTFE particle content, while few particle can be seen in FEGSEM images

Bath	tc	[wt.%]	[vol.%]	Bath	tc	[wt.%]	[vol.%]
4a	60	3.4	12.6	4d	30	3.3	12
	DC	3.3	12.2		60	3.8	13.7
4b	30	3.4	12.4	12.4		3.9	14.2
	60	4.1	14.7	4e	30	3.4	12.3
	DC	4.0	14.4		60	3.4	12.4
4c	30	3.7	13.3		DC	3.6	13
	60	3.6	13.1				
	DC	3.7	13.5				

7.2.3 Image analysis

Image analysis performed with images taken from the areas correspondingly to the areas assessed by EDX for comparison. The vol.% of PTFE particles and the error in measurements represented by the standard error deviation from image analysis are shown in **Table 7.3**, and it can be seen from these results that image analysis are close to the SEM cross section image results that shows few incorporated particles compare to the EDX results. Image analysis is not considered in this study as it gives an approximate analysis of the vol. % at the top surface and not consider a deeper depth and it was used for this composite just to give estimation about the particle inclusion and the behaviour of the produced coatings from different plating parameters.

tc[s]	30		60		DC, 3600	
Bath	V _{PTFE} [vol.%] SSD		V _{PTFE} [vol.%] SSD		V _{PTFE} [vol.%]	SSD
2a			0.0	0.0	0.0	0.0
2b	0.7	0.3	1.2	0.2	1.0	0.2
2c	0.3	0.0	0.5	0.3	0.4	0.1
2d	0.5	0.2	0.6	0.2	0.8	0.2
2e	0.4	0.1	0.6	0.2	0.5	0.1

Table 7-3: Image analysis results for bath B4 coatings shows low particle content similarly to the FEGSEM images analysis

7.2.4 Cathode efficiency

Cathode efficiency for the Co-PTFE coatings has been calculated similarly to the other nanocomposites coatings and using the vol. % calculated by image analysis and using the measured coatings thickness. The results are presented in **Figure 7.4**. Despite all the coatings showed comparable particle percent values, the cathode efficiency showed some variation among these coatings. Coatings produced by PRP demonstrate high cathode efficiency compared to the DC coatings. Lower duty cycle coatings have higher efficiency than the higher duty cycle coatings cathode efficiency value.

Also, coatings with no particle inclusions, performed with the highest cathode efficiency magnitude for PRP coatings, had a lower value than for the DC coating.



Figure 7-4: Cathode efficiency of Co-PTFE against tc for different SDS content used in this work.

7.2.5 XRD analysis

XRD patterns for all coatings showed a representative two peaks for cobalt in 100 and 110. No seen peak for PTFE in the patterns obtained by changing SDS content and duty cycle, **Figure 7.5** and **7.6**. Some change can be seen in both direction for all the coatings with increasing SDS content. Growth in 110 direction is noticeable with increasing the SDS while a decrement in 100 direction can be noticed, **Figure 7.5**. While the opposite behaviour can be seen with increasing duty cycle, **Figure 7.6**.



Figure 7-5: XRD patterns for Co-PTFE coatings of t_c= 60 s and different SDS content, the analysis performed using pure Si



Figure 7-6 XRD analysis of the Co-PTFE coatings produced from bathB4-b with different duty cycle

7.2.6 Discussion and Conclusion

SEM cross section, topography analysis, image analysis and XRD, from PRP and DC with different SDS content demonstrated that a low particles content achieved using the cobalt bath prepared in this study. On the contrary, EDX analysis showed higher PTFE particle content. The EDX results were excluded due to the missing evidence of the particles availability.

The particles content was low, with a similar value for all the different coatings. This suggests that the mechanism is not applicable for this system using the current plating parameters and bath composition. Also, FEGSEM images for the cross section showed smaller particle with 300 nm size compared to the original size of 1µm for the PTFE particles. This could to be the result of the effect of the ultrasound in breaking down the particle size into small particles. The DC coatings showed similar vol% of the particle as for PRP coatings. This suggests that other plating parameters need to be considered to achieve a good dispersion. Previous studies on the co-deposition of PTFE particles suggested that particle loading is playing an important role in incrementing the particle inclusion [139, 141]. Higher particle loadings produced coatings with higher particle content in both studies.

Investigating the bath composition effect (used cobalt bath, anionic surfactant, particle loading) should be taken into consideration in future work. Electroplating parameters and hydrodynamic effect should be also considered, as suggested in an earlier study [140].

CHAPTER 8: EFFECT OF INTRINSIC AND EXTRINSIC LENGTH SCALES ON THE MECHANICAL PROPERTIES OF ELECTROPLATED PURE COBALT AND COBALT NANOCOMPOSITES

8.1 Introduction

Indentation has long been a useful technique for measuring the mechanical properties of materials. It can give a single value for the hardness of the material using conical or pyramidal indenters. In this chapter microhardness indentation and nanoindenter tests using conical indenters, Knoop and Berkovich were performed to investigate the contribution of strengthening mechanisms, such as the particle dispersion and grain boundary effects, for the electroplated pure and nanocomposite Co-SiC and Co-Al₂O₃ produced by PRP. The strengthening of these nanocomposites has not been covered in the literature. The contribution of the strengthening mechanisms will be examined individually initially. A model which incorporates the combined effect of these mechanisms together is then constructed to give a better understanding of the relationship of the dispersion and grain size impact on the mechanical properties. The ISE is also investigated using a range of applied loads in the nanoindentation tests. The size effect is well-established in a number of micromechanical tests on mainly pure single crystalline materials [143]. In addition, a proposed relationship between hardness and wear resistance, H^3/E^2 is explored and the results of wear tests are presented to see if the performance enhancement suggested by the nanoindentation is realised in practice.

8.2 Results

8.2.1 Microhardness Indentation

Understanding the effects of the particle dispersion and grain boundary strengthening in the produced Co-SiC nanocomposites required considering the parameters of the electrochemical process on the resultant coatings. Hence, coatings from bath B-2 Co - SiC 0.2 g l⁻¹ SDS with particles loading (5-15) g l⁻¹ of 50nm SiC particles in the bath and

with different t_c will be considered. Coatings produced from baths B- 2b to B -2d or with loadings of 20 g l⁻¹ SiC or above are not investigated due to the high particle agglomeration observed in those coatings (see chapter six). Mechanical measurements of the Co-Al₂O₃ coatings are limited to SDS contents in the range of 0- 0.4 g l⁻¹ as coatings with higher SDS content were brittle, containing microcracks throughout the cross section, and are therefore not considered suitable candidates for further investigation. Coatings from bath 4 for the Co-PTFE are not investigated due to the low particle inclusion achieved in that system.

I. Microhardness of the Pure Cobalt and Co-SiC

8.2.1.1.1 Influence of microstructure

Figure 8.1 compares the microhardness of pure cobalt, produced from bath 1 with the same electroplating conditions as for the Co-SiC (with 0.2 g 1^{-1} SDS), with the microhardness of the Co-SiC coatings for different cathodic times, t_c. It is clear that pure Co showed no significant change in hardness with different t_c types, and that the microhardness of the Co-SiC coatings are always considerably higher than the equivalent Co coatings. The hardness value for the PRP Co coatings is in the range of 377- 382 HK (roughly equivalent to 373 HV or 3.658 GPa) and the microhardness of Co from DC is 366 HK. This hardness value is higher comparable with the hardness of 318HK (309.2 HV) for electroplated pure Co at 4A.dm⁻² and DC found in the literature [144] and also higher than the average hardness of electrodeposited hcp cobalt that reached 350HV~360 HK with 220nm crystalline size using the same current density [145]. For comparison with the hardness of Co-SiC the average value of the microhardness of 379.3 HK for the Co coatings produced by PRP will be used. The coatings produced by DC will not be further considered in this section, which will concentrate only on coatings produced by PRP.



Figure 8-1: Knoop microhardness against pure Co coatings and nanocomposite Co-SiC coatings with a bath loading of 5 g l⁻¹ SiC and 50 nm diameter particles.

Figure 8.2 shows the hardness of the Co-SiC coatings with different SiC contents. These were achieved using bath loadings in the range of 5-15 g l^{-1} SiC. The Co-SiC coatings all demonstrate a higher microhardness than the pure cobalt, with the microhardness generally increasing with the volume fraction of nanoparticles, with a peak hardness of 534 HK25g.



Figure 8-2: Microhardness of Co-SiC coatings from baths of different loadings of SiC content 5-15 g l⁻¹ against volume fraction of SiC nanoparticles

Figures 8.3 and **8.4** investigate the effect of crystallite size on microhardness. This displayed no noticeable change in values in both directions for the different cobalt grain sizes, although the change in crystallite size is small, in the range of 40-80 nm in either direction. This result indicates that the microhardness measurements are fairly independent of the Co crystallite size in the range of sizes achieved, which does not appear to be strongly influenced by the incorporation of Co-SiC particles in the range of 0- 8.7% volume fraction.



Figure 8-3: Microhardness of Co-nano SiC against crystallite size distributed in (100) direction.



Figure 8-4: Microhardness of Co-nano SiC against crystallite size distributed in (110) direction

8.2.1.1.2 A model of microhardness for nano-composite Co-SiC coatings

The interpretation of the contribution of the dispersion strengthening mechanisms in the resultant hardening of the nano Co-SiC will be presented in this section. Modelling of the indentation hardness of the pure Co and Co-SiC coatings presented in section 8.2.1 have been analysed using a least squares error minimisation fitting routine developed in Matlab. Equation (3.27) is adopted to fit the hardness data. The quality of the fit is shown in Figure 8.5. For the Co-SiC system the optimal values for the constants H_0 , A and B are determined, and the following hardness function (in HK 25gf) is obtained

$$H = 380.65 + \frac{2.226 * 10^{+4}}{L_p} + \frac{2.394 * 10^{-7}}{\sqrt{d}}$$
(8.1)

Where L_p is the average distance between SiC particles and *d* is the mean grain diameter in both directions for cobalt 100 and 110 calculated as explained in chapter six and seven. The magnitude of the intrinsic hardness H_0 is 380.65 HK25gf which is very close to the measured hardness of the produced electroplated pure cobalt 379.3 HK25gf. **Figure 8.5b** shows that the contribution from grain boundary strengthening is negligible, as the associated constant is $B=2.394*10^{-7}$. As shown in **Figure 8.5c**, the main contribution to hardening is the particle dispersed strengthening for which $A=2.226*10^{+4}$. Equation (3.27) is shown to effectively reproduce the trends in the data for particle content. The effect of grain size is negligible here, but that is probably due to the lack of variation in this parameter between coatings.



(a)



150



Figure 8-5: Least squares fit of equation (8.1) to hardness data for Co and Co-SiC coatings as a function of inverse particle spacing, $1/L_p$, and inverse root grain size, $1/\sqrt{d}$, (a) 3D view, (b) 2D aspect showing effect of grain size, (c) 2D aspect showing effect of particle spacing.

II. Co-Al₂O₃

A. Influence of microstructure

Alumina particles with a similar particle size to the SiC (45 nm) are expected to act in a similar way in terms of strengthening as they are both hard particles which will effectively block dislocation movement. **Figure 8.6** shows that the microhardness increases with increasing alumina particle volume fraction, with a peak value achieved at 540 HK25gf at 7.8 vol. % of Al₂O₃ (compared to 520 HK25g at 8.7 vol. % of SiC for the same SDS content of 0.4 g l⁻¹). The strengthening by the particles can be seen clearly in this figure. Comparing this plot with Co-SiC hardening due to the particle inclusion showed in **Figure. 8.2** revealed that the strengthening of Co-SiC due to the dispersed particles is linear, while for the nanocomposites Co-Al₂O₃ there is a step up before the linear trend. This difference could be attributed to the effect of the grain size refinement effect in this nanocomposites compared to the nanocomposites Co –SiC.

Figure 8.7 and **8.8** confirm that the hardness could be slightly increased by the reduction of the crystallites size for all the deposits of $Co-Al_2O_3$ although the trend is within the margins of error for the measurements. This indicates that the Co-matrix texture is not playing an essential role in the hardness for these nanocomposites.



Figure 8-6: Microhardness of Co-Al₂O₃ coatings from baths with 0-0.4 g l⁻¹ SDS content and t_c = 60-120 s against value fraction of 45 nm diameter nanoparticles.



Figure 8-7: Microhardness of Co-Al₂O₃ against grain size distributed in (100) direction.



Figure 8-8: Microhardness of Co-Al₂O₃ against grain size distributed in (110) direction.

Similarly, to the nano Co-SiC, the crystallite size of cobalt matrix for $Co-Al_2O_3$ nanocomposites is less than the spacing between the particles. This is probably why the particle incorporation is not reducing the crystallite size further, and why no significant increase in strengthening is expected from grain refinement in the PRP coatings above that achieved in the DC coatings.

8.2.1.1.3 A model of microhardness indentation for Co-Al₂O₃ nanocomposite coatings

• Surfactant loading of 0- 0.4 g l⁻¹ SDS

Following the method first introduced in section 8.2.1i, equation (3.27) is used to model the influence of microstructure on the hardness of Co-Al₂O₃ nanocomposites with surfactant loading in the range of 0- 0.4 g l⁻¹ SDS. **Figure 8.9** shows that the hardness trends are similar to those for SiC and are captured effectively by equation (3.27). In this case, the least squares fit generates a hardness function (in HK 25gf) with the following parameters given in the following equation (**equation 8.2**):

$$H = 398.3809 + \frac{2.321 * 10^{+04}}{L_p} + \frac{2.56 * 10^{-7}}{\sqrt{d}}$$
(8.2)

For Co-Al₂O₃ the intrinsic hardening H_0 is 398.3 HK which is still comparable to the 379.3 HK for the experimental data of pure Co. As shown in equation (8.2) and Figure 8.9b, the grain boundary strengthening contribution is minor, as found before for Co-SiC. Dispersion strengthening is the main contributing strengthening mechanism for this nanocomposite, with an approximately similar constant of $A = 2.321 \times 10^4$ as for Co-SiC.

Surfactant loading of 0.2- 0.4 g l⁻¹ SDS

I

The least squares fit generates a hardness function (in HK 25gf) with the following parameters in this case

$$H = 386.89 + \frac{2.5365 * 10^{+04}}{L_n} + \frac{1.0228 * 10^{-6}}{\sqrt{d}}$$
(8.3)





Figure 8-9 :Least squares fit of equation (8.2) to hardness data for Co and Co- Al₂O₃ coatings as a function of inverse particle spacing, $1/L_p$, and inverse root grain size, $1/\sqrt{d}$, (a) 3D view, (b) 2D aspect showing effect of grain size, (c) 2D aspect showing effect of particle spacing.

Surfactant loading of 0.2 g l⁻¹ SDS only

For direct comparison with the modelling results for the Co-SiC coatings, and the analysis is revisited using the same SDS content of 0.2 g l^{-1} only. The controlling strengthening mechanisms is still the particle dispersion as expected

$$H = 380.68 + \frac{2.67 * 10^{+04}}{L_p} + \frac{1.02 * 10^{-8}}{\sqrt{d}}$$
(8.4)

This result is compared with that of equation (8.1) for Co-SiC in section 8.2.1.

8.2.2 Nanoindentation Test

The previous microhardness tests have been undertaken at 25 gf using a Knoop indenter with a Mitutoyo model (MVK-G1) indentation machine. The theory of chapter three suggests that the internal strengthening length scales of the material influence the indentation size effect (ISE). Equation (3.26) predicts an ISE with an additional effect from the inverse sum length scale L_{eff} such that

$$H = H_0 + \Delta H \sqrt{1 + \frac{h^*}{h} + \frac{L^*}{L_{eff}}}$$
(8.5)

This is easily manipulated into the form

$$(H - H_0)^2 = A + \frac{B}{h}$$
(8.6)

where H_0 is the macroscopic hardness (also a function of L_{eff}), $A = \Delta H^2 \left(1 + \frac{L^*}{L_{eff}}\right)$ and $B = \Delta H^2 h^*$. This predicts a straight line with intercept A and slope B if $(H - H_0)^2$ is plotted against 1/h, where A is also a function of L_{eff} . It is this dependence which is of interest here.

The grain size length scale is roughly of the order of 40-80 nm and the particle spacing length scale in the composite coatings is 200 -300 nm. As the smallest length scale has the most influence on the strength, it is likely that the grain boundary strengthening, inherent in all coatings to a similar degree, will provide a substantial increase in hardness. The particle dispersion will contribute to the hardness in addition to this, depending on the particle content. The contribution of these length scales to the macroscopic hardness H_0 has been verified in the previous section. In this section, the presence of a contribution to the ISE through the forest hardening term A is also explored by investigating the hardness as a function of depth. Firstly, the hardness obtained by the macro and nano-indentation machines is compared at a similar load to verify they are giving a similar result. Then the ISE is investigated using nano-indentation data at lower loads.

I. Micro indentation-nanoindentation comparison

Hardness data from nanoindentation arrays on specimen cross sections are presented with results from tests on the macro-indentation machine using the same load 10 gf (100 mN). The two indenters have different tips, so some conversion of the nanoindentation hardness values into Knoop hardness is required. Indentation measurements were carried out on the Co-SiC nanocomposites produced by DC and PRP with 5 g l⁻¹ SiC producing coatings with 0 - 8.7 % volume fraction of nanoparticles without agglomeration. The tests were performed according to the method of Oliver and Pharr as described in chapter four. **Figure 8.10** shows that the results for all the coatings exhibit similar trends for both the micro and nano-indentation measurements. In addition, the nanoindentation values for the Co-SiC confirms the microhardness results for the effect of the dispersion on the resultant hardness.


Figure 8-10: Micro indentation and nanoindentation measurements for the Knoop hardness of pure cobalt and Co-SiC for different cathodic times 60-3600 s



Figure 8-11: micrograph of (i) Knoop and (ii) Berkovich indentations with 10 g or (mN) through the finished coating surface cross section with an average thickness 25 µm.

II. Indentation size effect

Nanoindentation test was achieved with loadings range 0-10 gf equivalent to 0-100 mN recorded in five steps to find the ISE contribution to the hardness. The forcedisplacement plots shown in **Figure 8.12** are for Co and Co-SiC produced under the same conditions. There is a visible change in the response with the incorporation of the

CHAPTER EIGHT: INTRINSIC AND EXTRINSIC LENGTH SCALES EFFECT ON THE MECHANICAL PROPERTIES OF Co AND Co NANOCOMPOSITES

nanoparticles into the cobalt matrix clearly increasing the indentation resistance of the sample.



Figure 8-12: Load-displacement plots for the electroplated Co and Co-SiC nanocomposites with the same electroplating conditions.

Figure 8.13 and **8.14** illustrate the utility of equation (8.6) for both Co-SiC and Co, where a straight line (represents the linear fitting) for $(H - H_0)^2$ with decreasing depth of indent for the cobalt with intercept shows some agreement with the predictions of the theory although there is substantial scatter in the data. Scatter is expected to increase as the homogeneity of the sample material decreases and the indentation depth decreases also. The fit for Co is A=0.8 GPa² and B=1.6 GPa² m. The fit for Co with SiC is A=0.123GPa² and = 4.25 GPa²m. The fit is not exceptionally good, although there is a fairly good trend if the very small indentation data is neglected. Overall it is difficult to draw any strong conclusions from this data due to the variability of the measurements.



Figure 8-13 Least square fitting for the Indentation size effect (ISE) data for Co electroplated nano-polycrystalline obtained by nanoindentation experiment. The straight line represents the linear fitting of all the produced coatings at different loading- indentation depth for the nanoindentation



Figure 8-14 Least square fitting for the Indentation size effect (ISE) data for Co-SiC electroplated nano-composites. The straight line represents the linear fitting of all the produced coatings at different loading- indentation depth for the nanoindentation

8.3 Discussion

It has been shown that increasing electrolyte loading of functionalized hard nanoparticles from 5 to 15 g l⁻¹ results in a proportional increase in hardness from 460 up to 530 HK25gf for Co-SiC, which is lower than the hardness of the hard chrome that is in the range of 600-1000 HV ~ 625-1055 HK [70]. Increasing SDS content in the electrolyte up to 0.4 g 1⁻¹ SDS results in improving the hardness number up to 560 HK25gf for the Co-Al₂O₃ nanocomposites. In the literature, it is typical for the increase in hardness with electrolyte loading particles to plateau or decrease at very high electrolyte loadings relating to nanoparticles agglomeration [17, 118]. Nanocomposite hardening with higher volume fractions is predicted by equations (8.1) and (8.3) for Co-SiC and Co-alumina. The crystallite size effect has been found to make no substantial contribution, mainly because this remains roughly constant across all samples. Figure 8.15 shows the predictions of the model for further increments in the particle volume fractions if achievable without agglomeration. The experimental data from 0.2 g l⁻¹ SDS Co-Al₂O₃ fits the model very well. The Co-SiC data also fits the model well, particularly data from the 5 g l^{-1} SiC particle bath loading. It is particularly encouraging that the models for the two systems are almost identical **Figure 8.16**. This is to be expected, as the SiC and alumina particles are of a 45 and 50 nm size and should play a similar role as obstacles to dislocation glide. The main difference between the two types of particles is their surface chemistry and the role of the surfactant in aiding their incorporation into the coatings during deposition. The additional extrinsic length scale strengthening contribution from the ISE is unclear from the results presented in Figures 8.13 and 8.14 due to unclear trend appearing. It is concluded that the main contribution to the intrinsic microstructural hardening effect is from the inclusion of nanoparticles.



Figure 8-15: Predicted hardness against particle volume fraction for Co-SiC and Co-Al₂O₃ using equation (8.4).



Figure 8-16: Predicted hardness against particle volume fraction for Co-SiC and Co-Al₂O₃ using equation (8.1)

8.4 Conclusion

- 1. Nanoparticles inclusion results in a significant increment of the hardening of the cobalt matrix, with 8.7 vol.% of SiC increasing the hardness by up to 25% and 9.1 vol% of Al_2O_3 raising it by up to 31% beyond the hardness of the pure Co coatings.
- 2. Surfactant content affect the hardness of the pure cobalt coatings and this should be considered when studying the mechanical properties of the electrodeposited nanocomposites in future.
- 3. A model for the main strengthening of the dispersion hardening is proposed for cobalt metal matrix nanocomposite with low anionic surfactant content 0.2 g l⁻¹ SDS and with average nanoparticle diameters of 45-50 nm. Good agreements of the experimental data found to fit the model.
- 4. The contribution of the grain boundary hardening is minor. The crystallite size is expected to contribute substantially to the hardness of the coatings, but as the crystallite size does not change significantly between coatings produced by different methods, the effect of changes in this parameter cannot be evaluated.
- 5. No significant effect of extrinsic length scale ISE can be seen for the both pure Co and Co-SiC with different depth of indentation.

CHAPTER 9: EFFECT OF HARDNESS AND ELASTIC MODULUS ON WEAR RESISTANCE

9.1 Introduction

Although hardness has long been considered as a main material property that can give indication about wear resistance, there is strong evidence to suggest that the elastic modulus can also have an important influence on wear behaviour. Specifically, the elastic strain to failure, which is related to the ratio of hardness (H) and elastic modulus (E), has been shown by many studies to be an important parameter for predicting wear resistance beyond hardness alone [146, 147]. In this work, nanoindentation tests were used to further examine the effect of the microstructure of cobalt and Co-SiC nanocomposites hard films, not only on the hardness of the coatings but also on the wear resistance. Leyland and Matthews (2000)[146] stated that good wear behaviour is typically characterised by a large elastic strain to failure. This can be given in terms of the ratio between the hardness H and the elastic modulus E as follow:

$$P_y = 0.78r^2 \left(\frac{H^3}{E^2}\right) \tag{9.1}$$

where P_y is the contact load at which the surface is yield in a rigid-ball on elastic/plastic plate contact and r is the contacting sphere radius. For hard coatings, H and E can easily be determined from loading-unloading curves measured by nano indentation and will be presented in the first section of this chapter. Pure cobalt and Co-SiC coatings with different vol. % and different cathodic times, $t_c = 60 - 3600$ s, were selected for the test. This produced nanocomposite coatings with vol. % in the range 0-8.7 vol. %. These measurements are the first for electroplated cobalt matrix nanocomposites and can be used to indicate the performance of these nanocomposites for applications that require high wear resistance. The second part of this chapter presents the results of wear test (pin on disc) for pure cobalt and Co-SiC with the same plating parameters presented in the first section (vol% 0 - 8.7).

9.2 Results of Nanoindentation

Nanoindentation test results from Chapter seven are used to examine the elastic modulus of the produced coatings with different nanoparticles dispersion and oxide availability. The elastic modulus of the coatings were shown to be approximately the same for the pure Co with t_c having little effect, see **Table 9.1**. A slight change in elastic modulus can be recognized by

increasing the SiC content of coatings with the increase in hardness of the nanocomposites because of the hard nanoparticles SiC. The obvious change in hardness for nanocomposite coatings, accompanied by no noticeable variation in elastic modulus. Few works considered the effect of the addition of nano SiC particles on the elastic modulus of a metal matrix and no works found on the effect of the nanoparticle inclusion on cobalt matrix. To gain insight into the expected wear resistance of these coatings, the measure $\frac{H^3}{E^2}$ from Equation.9.1 is plotted against t_c for both Co and Co-SiC in Figure 9.1. It is encouraging that there is a clear trend that the Co-SiC nanocomposites have the capacity to be more wear resistant than the pure Co coatings. Also, a recognised improvement with t_c is that the PRP results are better those from DC with higher resistance at low duty cycle seen with higher particles inclusion. These results suggest that coatings with lower duty cycle possess higher hardness and wear resistance.

Table 9-1: Mechanical parameters of Co and Co-SiC coatings showed the resistance to plasticdeformation of both coatings with 100 mN loading and for different t_c considering the standard deviationof the nanoindentation tests SSD

Coating	t _c (s)	H(GPa)	SSD	E(GPa)	SSD	$H^{3}/E^{2}(GPa)$
	60	4.001	0.20	207.95	25.70	0.00148
Pure Co	90	3.746	3.90	203	17.00	0.00128
	120	3.825	0.45	204.8	15.00	0.00133
	3600	3.560	0.37	201.9	20.00	0.00111
	60	4.874	0.06	202	35.00	0.00284
Co-SiC	90	4.472	0.62	204	25.00	0.00215
	120	4.511	0.60	203	25.15	0.00223
	3600	4.492	0.10	207	30.00	0.00212



Figure 9-1: Co and Co-SiC predicted wear resistance as a function of H³/E² for selected films of pure Co and Co-SiC with different cathodic time plating parameter. E is the elastic modulus of Co and Co-SiC measured by nanoindentation test

9.3 Results of Wear Test

The surface performance of the produced coatings are studied using pin on disc wear tests for selected electroplated cobalt nanocomposite samples and test conditions. The aim is to test the correlation with the predicted wear resistance H^3/E^2 from nanoindentation tests. Wear resistance depends not only on the properties of the tested materials but also on the overall characteristics of the tribological system, such as size, shape, roughness and hardness of the coatings (counter body), loading conditions, sliding speed and environment. In this work, the test conditions presented in chapter four where as a low load of 5 N was applied at a speed of 0.1 ms⁻¹ and a 500 m distance for all experiments; a track diameter of 25.4 mm was chosen. The measured surface roughness of the coating was measured. The average roughness was calculated and presented in **Table 9.2**. After each test, wear rate was calculated from the volume lost that was measured by 3D microscope from 5 different positions, as shown in **Table 9.2** with standard error deviation SSD for each measurement that reports the accuracy of these measurements.



iii) Typical line profile of a wear track measured by a surface 3D profiler after wear tests.

Figure 9-2: 3D representation of the wear scar and the method used to measure the volume lost in 3D microscope

The volume loss is given in **Table.9.2** and showed that Co nanocomposites produced by PRP have lower volume loss compared to pure cobalt. Coating produced by the lowest duty cycle, $t_c=60$ s and 8.7 vol.% showed the lowest volume loss among all the coatings, followed by the coating from $t_c=90$ s. DC Coating showed the highest volume loss compared to the othr Co-SiC electroplated layers. Wear rate of all the coatings from wear test for the selected experiments time was calculated by dividing the volume loss by the total distance (500 m) and applied load and plotted against tc to compare the results with the wear resistance prediction from nanoindentation test, **Figure 9.1** and **9.3**. The wear rate of the pure Co coating is showing a slight variation for different coatings produced by PRP and DC in a comparible behaviour as predicted by H³/E². Additionally, Co-SiC nanocomposites demonstrated much lower wear rate compared to the pure Co. The wear rate of the nanocomposites decreased with increasing the SiC nano particle content and decreasing duty cycle. This positively matches the predicted performance of the nanocomposites from H³/E².

Coatings	t _c (s)	$R_a(\mu m)$	SSD	Volume loss (m ³)	SSD	Wear rate (m ³ . N ⁻¹ . m ⁻¹)	COF
	60	0.1224	0.023	1.8 E*10 ⁻¹²	0.016	7.2*10 ⁻¹⁶	0.5290
Pure Co	90	0.1760	0.051	1.7*10 ⁻¹²	0.021	6.8*10 ⁻¹⁶	0.6534
	120	0.1823	0.034	2.0*10 ⁻¹²	0.023	8.0*10 ⁻¹⁶	0.6010
	3600	0.0643	0.065	2.1*10 ⁻¹²	0.031	8.4*10 ⁻¹⁶	0.7080
	60	0.2674	0.025	2.0*10 ⁻¹³	0.035	8.0*10 ⁻¹⁷	0.7420
Co-SiC	90	0.1974	0.012	7.5*10 ⁻¹³	0.033	3.0*10 ⁻¹⁶	0.7360
	120	0.2230	0.063	4.0*10 ⁻¹³	0.024	1.6*10 ⁻¹⁶	0.7730
	3600	0. 1224	0.0421	1.5*10 ⁻¹²	0.014	6.0*10 ⁻¹⁶	0.7940

Table 9-2: Coatings roughness, volume loss and Coefficient Of Friction (COF) for Co, and Co-SiC



Figure 9-3: Wear rate for Co and Co-SiC for different t_c

There are a limited number of reseach papers on Cobalt with nanoparticles, as shown in **Table 9.3**. Most of the work on nanocomposite cobalt and pure cobalt coatings is on the effectiveness of different techniques of electroplating. The table shows the wear rate of the coatings from the selected previous works compared to the current study, with the mean contact pressure for the wear tests in these works and the plating conditions used. From the table it can be seen that a pure cobalt coating from an earlier study by Weston [9] demonstrated a higher value $(7*10^{-14})$

 $m^3 N^{-1} m^{-1}$ compared to the pure cobalt in the current study with (8.4*10⁻¹⁶) $m^3 N^{-1} m^{-1}$. The mean contact pressure is approximately comparable to the current study. The difference in wear rate could be explained in terms of the plating conditions and surface roughness as the Co coating from the Weston et al study was 1µm, while in the current study it is 0.06 µm. No literature was found about the wear resistance of Co-SiC, hence the results are compared to the nanocomposities of cobalt matrix produced by different current techniques and to the results for Ni-SiC. The wear resistance of Ni-SiC with comparable mean contact pressure 0.56 GPa was found to be (7*10⁻¹⁴) m³ N⁻¹ m⁻¹, which is higher the value of the wear rate in the current study.

Coating	Mean contact pressure/ GPa	Wear rate / m ³ N ⁻¹ m ⁻¹	Electroplating conditions
Co [9]	0.659	7*10 ⁻¹⁴	DC plating
Co [145]	0.831	$3.5*10^{-14} - 4.25*10^{-14}$	PE plating
Co [148]	0.854	8.26*10 ⁻¹⁴	PE plating
Co-TiO2 [148]	0.854	7.5*10 ⁻¹⁴	PE plating
Ni-SiC[149]	0.56	7x10 ⁻¹⁴	DC with US
Co Current study	0.634	$8.4*10^{-16} - 7.2*10^{-16}$	DC-PRP with US
Co-SiC Current study	0.634	8*10* ⁻¹⁷ -6*10* ⁻¹⁶	DC-PRP with US

Table 9-3: Comparison of the wear results from the current work with the earlier studies

The values of the friction coefficient are presented in **Figures 9.4** and **9.5** for pure and Co-SiC coatings produced by DC and PRP for t_c =60 s. COF for pure cobalt showed higher values in DC compared to the PRP at t_c =60 s. This might be attributed to the effect of PRP and the coatings texture that was not discussed in this work. COF for the nanocomposite coatings is higher for the PRP coating at t_c =60 s compared to the DC coating. This could be explained due to the smooth surface of the DC coatings with less particles incorporated, resulting in lower friction between the two surfaces, **Figure 9.5**. Note that the friction cofficient for all of the coatings shows a smooth trend over the selected duration time.

Microscopic observation by SEM of the worn tracks for a selected coated sample are shown in **Figure 9.6**. The worn surface of the pure cobalt coatings showed two different regions, **Figure 9.6** i. The first region at the centre of the scar contains decapitated cobalt asperities with small

regions of oxidized cobalt filling the gaps in between. Similar results were reported in previous work for electroplated cobalt and in DC plating [9]. **Figure 9.6ii** shows the second region adjacent to the central track which involves a disrupted oxide material that corresponds to the regions of highest damage exhibited by the ball.

Co-SiC indicates that the worn surface contains some abrasive grooves resulting from the contact of the ball with the nanoparticles embedded in cobalt matrix, as can be seen in images **Figure 9.6 ii** and **iv** for Co-SiC with DC and $t_c= 60$ s respectively. Also, a dark film can be seen on the worn surface, **Figure 9.6 iv**, which was examined with EDX to investigate the oxygen availability.



Figure 9-4: Coefficient of friction $COF(\omega)$ for pure cobalt produced by PRP, tc=60s and DC



Figure 9-5: Coefficient of friction COF (ω) for Co-SiC produced by PRP, tc=60s and DC



Figure 9-6: (i, ii, iii, iv): SEM images of the worn surface of Co and Co-SiC
i) Worn surface of Co-DC coating ii) worn surface of Co-SiC-DC
iii) Worn surface of Co-PRP, t_c=60 s, iv) Worn surface of Co-SiC PRP, t_c=60 s

Compositional analysis by EDX of the worn surface are summarised in **Figure 9.7** for three different positions on the coatings surface. EDX analysis of the worn track shown in **Figure 9.7** i confirms the availability of an oxide layer of cobalt and no availability of Al elements transferred from the counter alumina ball to the coating surface. **Figure 9.7** ii Shows that much less oxygen was available on the coating surface far away from the wear track, reaching 4 at. %. Oxide/hydroxide availability with low values as was presented in chapter five. Also, some smooth area of the wear surface with cobalt oxide was available on the wear track surface. This indicates the availably of oxidative wear mechanism for these films, which could be accompanied by adhesive and abrasive wear. The alumina ball contact surface with the specimen showed no damaged surface and some transferred cobalt from the coating surface, as shown in **Figure 9.8**.

i)

Element	Weight%	Atomic%
O K Co K	20.83 79.17	49.22 50.78
Totals	100.00	



Liection in

ii)

Element	Weight%	Atomic%
O K Co K	2.00 98.00	4.00 96.00
Totals	100.00	



Figure 9-7: EDX analysis for the chemical composition of the worn surface of Co-SiC, $t_c = 60 \text{ s}$ i) Oxidative part of the scar, ii) Selected area of the coating surface





Figure 9-8: EDX analysis of the Alumina ball contact surface with the cobalt coatings from three different positions showed some cobalt at the contact area

9.4 Discussion

Combining the measurement of hardness H and elastic modulus E in indentation tests, the predicted wear resistance showed that coatings with the lower duty cycle have a promisingly higher wear resistance. The wear rate calculated from the pin on disc tests confirmed this finding, where the coating with the highest SiC vol. %, hardness, and H^3/E^2 ratio, demonstrates the lowest volume loss in the wear test. This is expected to partly arise from the good particle dispersion achieved by PRP and SDS anionic surfactant with the shortest t_c that makes the SiC hinder grain movement and grain boundary migration during sliding, reducing volume loss [23, 148]. The effect of the duty cycle has been explored. The H^3/E^2 ratio for coatings produced with $t_c = 90$ s than that for the coating with $t_c = 120$ s, whereas the particle volume fraction of the $t_c = 90$ s coating is lower than that for the $t_c = 120$ s case, with values of 4.7 % and 6.4 % respectively. This indicates that wear resistance is not just due to the particles inclusion level. This is confirmed also by the volume loss in the pin on disc tests. This suggests that both of the elastic modulus and hardness test in nanoindentation measurements can be used for the prediction of the wear resistance of the cobalt electroplated coatings, taking into consideration the difficulites to perform the indentation for a small size of about 25 µm of the cross section of the coatings surface.

9.5 Conclusions

In the present study, nano-crystalline Co and Co/SiC nano-composites were produced by pulse reverse electrodeposition, and their hardness, elastic of modulus and wear rate together with their morphology, were examined. The outcome of the results can be summarized as follows:

1. H^3/E^2 can be used as a reliable indicator of the wear resistance of Co/ Co-SiC. The lowest wear resistance was for DC coatings among all the Co-SiC electroplated specimens tested. The volume loss of the cobalt decreased by about 4, 3 and 2 times after Co-deposition of SiC into Co matrix by PRP and with t_c= 60 s, 90 s, and 120 s respectively.

Pure Co coatings produced by DC demonstrated higher friction coefficients compared to the PRP coatings. Co-SiC coatings produced by DC have a higher COF compared to those produced by PRP.

CHAPTER 10: DISCUSSION

10.1 Particles inclusion mechanisms

Both nanocopmosites of Co-SiC of the present and the previous work, and Co-Al₂O₃ achieved the highest particles content at low duty cycles. The attained particles content in Co-nano SiC was higher compared to the Co - nano Al_2O_3 . Also, it can be seen that particles increased significantly in coatings of Co-SiC with the surfactant addition. Surfactant addition to the cobalt in Co - Al₂O₃ system showed some particle increase with the surfactant addition, but less compared to the nano Co-SiC coatings particles incorporation. Further increase in surfactant content in Co-SiC system from the previous work [78] resulted in the highest SiC particles content at SDS content of 0.6 g l^{-1} with ~18.4 vol.% at $t_c = 30$ s. This is suggested to be resulted by the particles characteristics from both systems, where more information about the zeta potential and surface charge can explain the particles adsorption to the anionic surfactant and their movement through the electroplating bath to be captured at the working electrode surface. Lee and Wan worked on Cu- γ - Al₂O₃ system and showed that the zeta potential of γ -Al₂O₃ particles in copper sulphate solution (<0.1 M) is negative. Assuming that the zeta potential of alumina particles in cobalt bath in this study was negative that less surfactant could adsorped and hence confer less negative surface charge compared to the SiC in Co-SiC system.

PTFE particles incorporation into cobalt matrix was limited for smaller particles in DC and PRP plating that reached 300nm. The particles with that size were expected to be resulted by the ultrasound effect of breaking down the particles. The limited inclusion might indicate the mechanical entrapment of the particles in DC is low in this bath. The PRP with the anionic surfactant is not working for the 1 µm PTFE particles surface chemistry.

10.2 MECHANICAL PROPERTIES

Increasing the particles inclusion up to certain point led to increase the hardness of the nanocomposites. Beyond a certain point of the particles inclusion a decrease in the hardness number were seen for the Co-SiC with different SDS content. This could be explained due to the brittleness in the coatings resulted by the high vol. % of the hard ceramic particles. The predicted model for both nanocopmosites showed that the hardness of the nanocomposites are expected to reach a certain hardness number then high particle content might result in coating brittleness. Hence, the plots could be restricted to lower particles inclusion and lower achieved

microhardness as shown in **Figure. 10.1**, and **Figure. 10.2**. According to these plots, it is predicted that Co - SiC and Co - Al_2O_3 with 20 vol. % can enhance the coating hardness resulting in a 1000 - 1200 HK for the produced nanocomposites by this mechanism. This expects that the cobalt nanocomposites in this work can be served as a good replacement for the hard chrome.



Figure 10-1 Predicted hardness against particle volume fraction up to 20 vol. % for Co-SiC and Co-Al₂O₃ using equation (8.4).



Figure 10-2 Predicted hardness for both nanocomposites of Co-SiC and Co-Al₂O₃ using equation (8.5)

CHAPTER 11: CONCLUSION AND FUTURE WORK

11.1 Conclusion

11.1.1 PRP and an anionic surfactant technique for cobalt systems of Co-SiC and Co-Al₂O₃

- 1. PRP technique can be used successfully to produce nanocomposites coatings with higher particle inclusion than DC plating
- 2. Uniform dispersion can be achieved by using PRP and an anionic surfactant with 5 g. I^{-1} with different SDS content of 0.2 0.8 g I^{-1} for Co-SiC and Co Al₂O₃ nanocomposites. Brittle coatings are produced beyond 0.4 g I^{-1} , which restricts the use of the surfactant beyond 0.4 g I^{-1} .
- 3. PRP with the anionic surfactant technique is applicable for higher particle loading in Co-SiC up to 15 g l⁻¹ and with 0.2 g l⁻¹ SDS where a good dispersion through the coatings cross section with few agglomerated particles and a maximum particle content of 9 % vol was achieved.
- 4. Increasing particle loading decreases the electrophoretic effect that accompanies the PRP and anionic surfactant, and increases the effect of the mechanical entrapment. This effect was verified with increasing $t_c = 60-120$ s.
- 5. Co-Al₂O₃ nanocomposites performed similarly to the Co-SiC with 0.2 g l⁻¹ SDS, where higher particle content achieved with lower duty cycle and t_c = 30 s and 40 s for these nanocomposites.
- 6. The particle number captured by each cycle was calculated for Co SiC and Co -Al₂O₃. A similar trend of behaviour was shown which suggests the ability of generalising a model for the particle behaviour for the specific plating parameters and conditions used in this work.
- Very few particles were incorporated for Co-PTFE with 1 μm particle size, which suggests that PRP and anionic surfactant co-electrodeposition mechanism is difficult for this surface chemistry of the PTFE with 1 μm.
- Nanoparticle inclusion resulted in a grain size a slight reduction in the cobalt matrix in both Co – SiC and Co - Al₂O₃ nanocomposites with increasing particle content 1-9 vol.

%. The grain size reduction range was 50-100 nm for Co-SiC with 5 - 15 g l^{-1} and 60 - 120 nm for Co - Al₂O₃ with 0 - 0.8 g l^{-1} SDS.

9. TEM analysis was used to investigate the grain size of Co, and spacing between nanoparticles and their dispersion through cobalt matrix. The analysis confirmed the XRD results of the calculated grain size of the cobalt matrix. The spacing between the particles for the selected specimen with 8.7 vol % was 100 - 200 nm. Additionally, the TEM observations showed a decent particle dispersion of the particles through the Co.

11.1.2 Mechanical behaviour of the electroplated cobalt nanocomposites

- Microhardness measurements were performed for the coatings with no agglomeration and no cracks from Co-SiC with 5-15 g l⁻¹ SiC and 0.2 g l⁻¹ SDS and for Co - Al₂O₃ with 5 g l⁻¹ SiC and 0- 0.4 g l⁻¹ SDS. The results showed that the microhardness number increased significantly with increasing particle vol. % maximising at about 25% and 31% for Co - SiC and Co - Al₂O₃ beyond the hardness of pure cobalt.
- 2. The main contributing strengthening is due to the nanoparticle dispersion.
- 3. A predicted model was found for both nanocomposites of Co SiC and Co Al₂O₃ produced by PRP and SDS of 0.2 g l⁻¹ for the used electroplating conditions. Good agreement was found between the experimental data and the model.
- 4. Nanoindentation was used to investigate the hardening effect not only by considering the intrinsic size effect but also the extrinsic size effect caused by ISE. The results suggested no significant contribution of the ISE.
- 5. Nanoindentation was used additionally to predict the wear resistance behaviour using hardness and elastic modulus of the coatings according to the term H³/E². The predicted results suggested that coatings with 60 s, 90 s, and 120 s have higher wear resistance compared to the DC coating.
- 6. The wear rate of the nanocomposites coatings followed a pattern of behaviour that confirms the predicted behaviour using H^3/E^2 and suggests that the coatings with the lower duty cycle from 0.2 g l⁻¹ SDS have the lowest value. This finding showed that the particle inclusion from low duty cycle predicted by the suggested PRP and SDS mechanism accompanied with the low elastic modulus can enhance the wear resistance of the well dispersed nano cobalt composites.

11.2 Future work

- 1. Further work is needed to eliminate the effect of anodic dissolution at low duty cycle as high particle content can be achieved with that lower duty cycle.
- 2. More analysis is required to understand the behaviour of the included particles, which can be done by considering the zeta potential measurements to understand the surface charge. Also, XPS analysis should be performed for different SDS content to understand the effect of the anionic surfactant on the coatings composition.
- 3. All the plating parameters should be precisely considered to achieve consistency and repeatability of all the results.
- 4. Using a larger substrate dimension to overcome the delamination problems caused by sample handling and microstructural examinations preparations.

REFERENCES

- 1. Boyer, H.E. and T.L. Gall, Metals Handbook, ASM, Metals 1985, Park, Ohio
- 2. Dennis, J.K. and T.E. Such, *Nickel and Chromium Plating*. 1993: Woodhead Publishing.
- Cushnie, G.C., *Pollution Prevention and Control Technologies for Plating Operations*.
 2009: George Cushnie.
- Rastegar, F. and D.E. Richardson, *Alternative to chrome: HVOF cermet coatings for high horse power diesel engines*. Surface and Coatings Technology, 1997. **90**(1–2): p. 156-163.
- 5. Facchini, D., et al. *Electrodeposition of nanocrystalline cobalt alloy coatings as a hard chrome alternative.* in *DoD Corrosion Conference.* 2009.
- 6. Uwe Erb, K.T.A., and Gino Palumbo, in *NANOSTRUCTURED MATERIALS Processing, Properties and Potential Applications*, N.C.N.P. North Carolina State University Raleigh, Editor. 2002, WILLIAM ANDREW: Norwich, New York, U.S.A.
- Podlaha, E.J., Selective electrodeposition of nanoparticulates into metal matrices. Nano letters, 2001. 1(8): p. 413-416.
- 8. Erb, U., *Electrodeposited nanocrystals: Synthesis, properties and industrial applications.* Nanostructured Materials, 1995. **6**(5): p. 533-538.
- 9. Weston, D.P., et al., Friction and sliding wear behaviour of electrodeposited cobalt and cobalt–tungsten alloy coatings for replacement of electrodeposited chromium. Wear, 2009. 267(5-8): p. 934-943.
- Alkire, R.C., et al., Advances in Electrochemical Science and Engineering. 2008: Wiley.

- 11. Ioury Timoshkov, Victor Kurmashev, and V. Timoshkov, *Electroplated Nanocomposites of High Wear Resistance for Advanced Systems Application*. 2011.
- 12. Mellor, B.G., *Plating and Surface Finishing*. 1999: American Electroplaters' Society.
- 13. Balasubramanian, M., Composite Materials and Processing. 2013: CRC Press.
- 14. Gomes, A., et al., *Electrodeposition of metal matrix nanocomposites: improvement of the chemical characterization techniques*. 2011: INTECH Open Access Publisher.
- Chandrasekar, M.S. and M. Pushpavanam, *Pulse and pulse reverse plating— Conceptual, advantages and applications*. Electrochimica Acta, 2008. 53(8): p. 3313-3322.
- Weston, D., et al., Co-electrodeposition of inorganic fullerene (IF-WS 2) nanoparticles with cobalt from a gluconate bath with anionic and cationic surfactants. Electrochimica Acta, 2011. 56(19): p. 6837-6846.
- 17. Nasirpouri, F., *Electrodeposited Nanocomposite Films*, in *Electrodeposition of Nanostructured Materials*. 2017, Springer International Publishing: Cham. p. 289-310.
- Hovestad, A. and L.J. Janssen, *Electroplating of metal matrix composites by codeposition of suspended particles*. Modern aspects of electrochemistry, 2005. 38: p. 475.
- 19. Walsh, F. and C. Ponce de Leon, *A review of the electrodeposition of metal matrix composite coatings by inclusion of particles in a metal layer: an established and diversifying technology.* Transactions of the IMF, 2014. **92**(2): p. 83-98.
- Low, C., R. Wills, and F. Walsh, *Electrodeposition of composite coatings containing nanoparticles in a metal deposit.* Surface and Coatings Technology, 2006. 201(1-2): p. 371-383.

- 21. Mishra, R., B. Basu, and R. Balasubramaniam, *Effect of grain size on the tribological behavior of nanocrystalline nickel*. Materials Science and Engineering: A, 2004. 373(1-2): p. 370-373.
- 22. Sun, X. and J. Li, *Tribological characterisation of electrodeposited nickel-titania* nanocomposite coatings sliding against silicon nitride in high vacuum. Surface Engineering, 2008. **24**(3): p. 236-239.
- 23. Sun, X.J. and J.G. Li, *Friction and Wear Properties of Electrodeposited Nickel–Titania Nanocomposite Coatings*. Tribology Letters, 2007. **28**(3): p. 223-228.
- Vaezi, M.R., S.K. Sadrnezhaad, and L. Nikzad, *Electrodeposition of Ni–SiC nano*composite coatings and evaluation of wear and corrosion resistance and electroplating characteristics. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. 315(1): p. 176-182.
- 25. Zimmerman, A., et al., *Pulse electrodeposition of Ni–SiC nanocomposite*. Materials letters, 2002. **52**(1-2): p. 85-90.
- Guglielmi, *Kinetics of the deposition of inert particles from electrolytic baths*. Journal of the Electrochemical Society., 1972. 8.
- 27. Frasaer, C., and Roos Analysis of the electrolytic codeposition of non-Brownian particles with metals. Electrochem.Soc, 1992. **139**(413-25).
- 28. Hovestad, A. and L. Janssen, *Electrochemical codeposition of inert particles in a metallic matrix*. Journal of Applied Electrochemistry, 1995. **25**(6): p. 519-527.
- 29. Hwang, B.J. and C.S. Hwang, *Mechanism of codeposition of silicon carbide with electrolytic cobalt.* Journal of the Electrochemical Society, 1993. **140**(4): p. 979-984.
- Celis, J.-P., J. Roos, and C. Buelens, A mathematical model for the electrolytic codeposition of particles with a metallic matrix. Journal of the Electrochemical Society, 1987. 134(6): p. 1402-1408.

- Vereecken, S.I. and J. Searson P.C., *Quantifying Electrochemical Nucleation and Growth of Nanoscale Clusters Using Real-Time Kinetic Data*. Electrochem. Soc, 2002. 147(7).
- 32. Brandes, E. and D. Goldthorpe, *Electrodeposition of cermets*. Metallurgia, 1967.
 76(457): p. 195-198.
- 33. Meguro, K., et al., *Effects of surfactants and surface treatment on aqueous dispersion of silicon carbide*. Bulletin of the Chemical Society of Japan, 1987. **60**(1): p. 89-94.
- 34. Güler, E.S., *Effects of Electroplating Characteristics on the Coating Properties*, in *Electrodeposition of Composite Materials*. 2016, InTech.
- 35. Greco, V. and W. Baldauf, *Electrodeposition of Ni-Al 2 O 3, Ni-TiO 2 and Cr-TiO 2 dispersion hardened alloys.* Plating, 1968. **55**(3): p. 250-257.
- Afshar, A., M. Ghorbani, and M. Mazaheri, *Electrodeposition of graphite-bronze* composite coatings and study of electroplating characteristics. Surface and Coatings Technology, 2004. 187(2-3): p. 293-299.
- Foster, J. and B. Cameron, *The effect of current density and agitation on the formation of electrodeposited composite coatings*. Transactions of the IMF, 1976. 54(1): p. 178-183.
- Gamburg, Y.D. and G. Zangari, *Theory and Practice of Metal Electrodeposition*. 2011: Springer New York.
- 39. Yang, Z., et al., *The fabrication and corrosion behavior of electroless Ni–P-carbon nanotube composite coatings*. Materials Research Bulletin, 2005. **40**(6): p. 1001-1009.
- 40. Lee, H.-K., H.-Y. Lee, and J.-M. Jeon, *Codeposition of micro- and nano-sized SiC particles in the nickel matrix composite coatings obtained by electroplating*. Surface and Coatings Technology, 2007. **201**(8): p. 4711-4717.

- 41. Hunter, R.J., R.H. Ottewill, and R.L. Rowell, *Zeta Potential in Colloid Science: Principles and Applications*. 2013: Elsevier Science.
- 42. Shrestha, N.K., M. Masuko, and T. Saji, *Composite plating of Ni/SiC using azo-cationic surfactants and wear resistance of coatings*. Wear, 2003. **254**(5-6): p. 555-564.
- 43. Shrestha, N.K., I. Miwa, and T. Saji, *Composite plating of Ni/SiC using a cationic surfactant with an azobenzene group*. Journal of the Electrochemical Society, 2001.
 148(2): p. 106-109.
- Sabri, M., A.A. Sarabi, and S.M.N. Kondelo, *The effect of sodium dodecyl sulfate surfactant on the electrodeposition of Ni-alumina composite coatings*. Materials Chemistry and Physics, 2012. **136**(2-3): p. 566-569.
- 45. Kim, S.K. and H.J. Yoo, *Formation of bilayer Ni–SiC composite coatings by electrodeposition*. Surface and coatings Technology, 1998. **108**: p. 564-569.
- 46. Kuo, S.L., *The influence of process parameters on the MoS2 content of Ni-MoS2 composite coating by the robust design method.* Journal of the Chinese Institute of Engineers, 2004. **27**(2): p. 243-251.
- Verelst, M., J. Bonino, and A. Rousset, *Electroforming of metal matrix composite:* dispersoid grain size dependence of thermostructural and mechanical properties. Materials Science and Engineering: A, 1991. 135: p. 51-57.
- 48. Sautter, F., *Electrodeposition of Dispersion-Hardened Nickel-Al2 O 3 Alloys*. Journal of the electrochemical society, 1963. **110**(6): p. 557-560.
- 49. Walsh, F. and K. Helle, *Electrodeposition of composite layers consisting of inert inclusions in a metal matrix.* Transactions of the IMF, 1997 **75**(2): p. 53-58.
- 50. Tudela, I., et al., *Ultrasound-assisted electrodeposition of composite coatings with particles*. Surface and Coatings Technology, 2014. **259**: p. 363-373.

- 51. Gyawali, G., et al., *Pulse electrodeposition and characterisation of Ni–SiC composite coatings in presence of ultrasound*. Transactions of the IMF, 2012. **90**(5): p. 274-281.
- Tudela, I., et al., Ultrasound-assisted electrodeposition of thin nickel-based composite coatings with lubricant particles. Surface and Coatings Technology, 2015. 276: p. 89-105.
- 53. García-Lecina, E., et al., A comparative study of the effect of mechanical and ultrasound agitation on the properties of electrodeposited Ni/Al 2 O 3 nanocomposite coatings. Surface and Coatings Technology, 2012. 206(11): p. 2998-3005.
- Cojocaru, P., A. Vicenzo, and P.L. Cavallotti, *Electrodeposition of Au/nanosized diamond composite coatings*. Journal of Solid State Electrochemistry, 2005. 9(12): p. 850-858.
- Walsh, F., C. Low, and J. Bello, *Influence of surfactants on electrodeposition of a Ni*nanoparticulate SiC composite coating. Transactions of the IMF, 2015. **93**(3): p. 147-156.
- 56. Burzyńska, L., et al., *Electrodeposition and heat treatment of nickel/silicon carbide composites*. Surface and Coatings Technology, 2008. **202**(12): p. 2545-2556.
- Mandich, N., *Pulse and pulse-reverse electroplating*. Metal Finishing, 1999. 97(1): p. 375-380.
- 58. Feng Wang, Susumu Arai a, and M. Endo, *Preparation of nickel–carbon nanofiber* composites by a pulse-reverse electrodeposition process. 2007.
- 59. Puippe, J.-C. and F. Leaman, *Theory and practice of pulse plating*. 1986: Amer Electroplaters Soc.
- Roy, S. and D. Landolt, *Determination of the practical range of parameters during reverse-pulse current plating*. Journal of Applied Electrochemistry, 1997. 27(3): p. 299-307.

- 61. Panda, A. and E. Podlaha, *Nanoparticles to improve mass transport inside deep recesses*. Electrochemical and solid-state letters, 2003. **6**(11): p. 149-152.
- 62. Podlaha, E. and D. Landolt, *Pulse-Reverse Plating of Nanocomposite Thin Films*. Journal of The Electrochemical Society, 1997. **144**(7): p. 200-202.
- 63. Feng Wang a, Susumu Arai a, and M. Endo, *Preparation of nickel–carbon nanofiber composites by a pulse-reverse electrodeposition process*. Electrochemistry Communications, 2007. **7**(7): p. 674-678.
- 64. Wang, F., S. Arai, and M. Endo, *Electrochemical preparation and characterization of nickel/ultra-dispersed PTFE composite films from aqueous solution*. Materials transactions, 2004. **45**(4): p. 1311-1316.
- 65. Tai WP, Kim YS, and K. JG., *Fabrication and magnetic properties of Al2O3/Co nanocomposites*. Materials Chemistry and Physics, 2003. **82(2)**: p. 396-400.
- 66. Kosta, I., M. Sarret, and C. Müller, *Structure, microhardness and corrosion behaviour of nanostructured CoP coatings obtained by direct current and pulse plating.* Electrochimica Acta, 2013. **114**: p. 819-826.
- Baghal, S.L., et al., The effect of SDS surfactant on tensile properties of electrodeposited Ni–Co/SiC nanocomposites. Materials Science and Engineering: A, 2013. 559: p. 583-590.
- Roos, J., et al., *The development of composite plating for advanced materials*. JOM Journal of the Minerals, Metals and Materials Society, 1990. 42(11): p. 60-63.
- 69. Rudnik, E., L. Burzyńska, and W. Jakubowska, *Codeposition of SiC particles with cobalt matrix*. ISSUES, 2010. 1: p. 2.
- Lausmann, G., *Electrolytically deposited hardchrome*. Surface and Coatings Technology, 1996. 86: p. 814-820.

- 71. Gladman, T., *The physical metallurgy of microalloyed steels*. Vol. 615. 1997: Maney Pub.
- 72. Morris, J.W., Dislocation plasticity: overview 2016.
- 73. Queyreau, S., G. Monnet, and B. Devincre, Orowan strengthening and forest hardening superposition examined by dislocation dynamics simulations. Acta Materialia, 2010. 58(17): p. 5586-5595.
- 74. William D. Callister, J., *Materials Science and Engineering*. 2007, New York: John willey & Sons, Inc.
- 75. Pharr, G.M., E.G. Herbert, and Y. Gao, *The indentation size effect: a critical examination of experimental observations and mechanistic interpretations*. Annual Review of Materials Research, 2010. **40**: p. 271-292.
- Gao, H. and Y. Huang, *Geometrically necessary dislocation and size-dependent plasticity*. Scripta Materialia, 2003. 48(2): p. 113-118.
- Nix, W.D. and H. Gao, *Indentation size effects in crystalline materials: A law for strain gradient plasticity*. Journal of the Mechanics and Physics of Solids, 1998. 46(3): p. 411-425.
- 78. Weston, D.P., *Electrodeposition of Nanocomposite Metallic Coatings*, in *Electrochem* 2014: Loughborough. p. 25.
- McClelland, J.J., et al., *Bright focused ion beam sources based on laser-cooled atoms*.Applied physics reviews, 2016. 3(1): p. 011302.
- Giannuzzi, L.A. and F.A. Stevie, A review of focused ion beam milling techniques for TEM specimen preparation. Micron, 1999. 30(3): p. 197-204.
- Langford, R. and A. Petford-Long, *Preparation of transmission electron microscopy cross-section specimens using focused ion beam milling*. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 2001. 19(5): p. 2186-2193.

- 82. Young, R., et al. High-yield and high-throughput TEM sample preparation using focused ion beam automation. in Istfa'98: Proceedings of the 24Th International Symposium for Testing and Failure Analysis. 1998. ASM International.
- Dinnebier, R.E. and S.J.L. Billinge, *Powder Diffraction: Theory and Practice*. 2008: Royal Society of Chemistry.
- 84. Gubicza, J., X-Ray Line Profile Analysis in Materials Science. 2014: IGI Global.
- Scardi, P., M. Leoni, and R. Delhez, *Line broadening analysis using integral breadth methods: a critical review*. Journal of Applied Crystallography, 2004. **37**(3): p. 381-390.
- Gubicza, J. and T. Ungár, *Characterization of defect structures in nanocrystalline materials by X-ray line profile analysis*. Zeitschrift f
 ür Kristallographie-Crystalline Materials, 2007. 222(11/2007): p. 567-579.
- 87. Bertaut, E., *Structures des boroferrites*. Acta Crystallographica, 1950. **3**(6): p. 473-474.
- Louër, D., et al., A precise determination of the shape, size and distribution of size of crystallites in zinc oxide by X-ray line-broadening analysis. Journal of Applied Crystallography, 1983. 16(2): p. 183-191.
- 89. Koch, C., et al., *Structural Nanocrystalline Materials: Fundamentals and Applications*.
 2007: Cambridge University Press.
- 90. Klug, H. and L. Alexander, X-ray Diffraction. 1974, John Wiley and Sons

USA.

- 91. Pecharsky, V. and P. Zavalij, *Fundamentals of Powder Diffraction and Structural Characterization of Materials, Second Edition.* 2008: Springer US.
- 92. Guinebretière, R., X-Ray Diffraction by Polycrystalline Materials. 2013: Wiley.

- 93. Thorne, A., U. Litzén, and S. Johansson, *Spectrophysics: Principles and Applications*.
 1999: Springer Berlin Heidelberg.
- 94. Carberry, *Chemical Reaction and Reactor Engineering*. 1986: Taylor & Francis.
- 95. Mittemeijer, E. and R. Delhez, *Accuracy in powder diffraction*. NBS Special Publ, 1980. **567**: p. 271-314.
- 96. Mittemeijer, E.J. and P. Scardi, *Diffraction Analysis of the Microstructure of Materials*.
 2013: Springer Berlin Heidelberg.
- 97. Mendenhall, M., *Powder Diffraction SRMs*. Journal of Alloys and Compounds, 2016.
 590: p. 294-302.
- 98. Uvarov, V. and I. Popov, *Metrological characterization of X-ray diffraction methods at different acquisition geometries for determination of crystallite size in nano-scale materials*. Materials Characterization, 2013. **85**: p. 111-123.
- Debye, P. and P. Scherrer, *Atombau*. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse, 1918. 1918: p. 101-120.
- Langford, J.I. and A.J.C. Wilson, Scherrer after sixty years: A survey and some new results in the determination of crystallite size. Journal of Applied Crystallography, 1978. 11(2): p. 102-113.
- 101. Roy R, Roy RA, and R. DM, *Alternative perspectives on "quasi-crystallinity": non-uniformity and nanocomposites*. Materials Letters, 1986. **4(8-9)**: p. 323-328.
- 102. Patterson, A., *The Scherrer formula for X-ray particle size determination*. Physical review, 1939. **56**(10): p. 978.
- 103. Chandler, H. and A. International, *Hardness Testing*, 2nd Edition. 1999: ASM International.

- 104. Dieter, G.E. and D. Bacon, Mechanical Metallurgy. 1988: McGraw-Hill.
- 105. Smallman, R.E. and R.J. Bishop, *Modern Physical Metallurgy and Materials* Engineering: Science, Process, Applications. 1999: Butterworth-Heinemann.
- 106. Oliver, W.C. and G.M. Pharr, *An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments.* Journal of materials research, 1992. **7**(6): p. 1564-1583.
- 107. Amanieu, H.-Y., et al., Mechanical property measurements of heterogeneous materials by selective nanoindentation: Application to LiMn2O4 cathode. Materials Science and Engineering: A, 2014. 593: p. 92-102.
- 108. Ivanov, E., et al., *Experimental Nano and Micro Mechanics of Nanostructured Materials*. 2012. Part IV, Chapter 3, pp. 287-326.
- Bowden, F.P. and D. Tabor, *The friction and lubrication of solids*. Vol. 1. 2001: Oxford university press.
- Maurin, G. and A. Lavanant, *Electrodeposition of nickel/silicon carbide composite coatings on a rotating disc electrode*. Journal of Applied Electrochemistry, 1995.
 25(12): p. 1113-1121.
- Juneghani, M.A., M. Farzam, and H. Zohdirad, Wear and corrosion resistance and electroplating characteristics of electrodeposited Cr–SiC nano-composite coatings.
 Transactions of Nonferrous Metals Society of China, 2013. 23(7): p. 1993-2001.
- 112. Larson, C. and J. Farr, *Current research and potential applications for pulsed current electrodeposition–a review*. Transactions of the IMF, 2012. **90**(1): p. 20-29.
- 113. Larson, C. and J. Farr, *Recent advances in pulsed current electrodeposition: a brief review*. Transactions of the IMF, 2010. **88**(5): p. 237-242.

- 114. Zhang, Z. and D.L.A. Chen, Consideration of Orowan strengthening effect in particulate-reinforced metal matrix nanocomposites: A model for predicting their yield strength. . Scripta Materialia, 2006. 54: p. 1321–1326.
- 115. Rastogi, R., et al., *Comparative study of carbon nanotube dispersion using surfactants*.Journal of colloid and interface science, 2008. **328**(2): p. 421-428.
- 116. Weston, D.P., et al., *Establishing relationships between bath chemistry, electrodeposition and microstructure of Co–W alloy coatings produced from a gluconate bath.* Electrochimica Acta, 2010. **55**(20): p. 5695-5708.
- 117. Baldwin, P.C., Some unfamiliar aspects of pulse plating. Metal Finishing, 1995. 93(6):p. 84-86.
- Borkar, T. and S.P. Harimkar, *Effect of electrodeposition conditions and reinforcement content on microstructure and tribological properties of nickel composite coatings*. Surface and Coatings Technology, 2011. 205(17-18): p. 4124-4134.
- Thiemig, D., R. Lange, and A. Bund, *Influence of pulse plating parameters on the electrocodeposition of matrix metal nanocomposites*. Electrochimica Acta, 2007. 52(25): p. 7362-7371.
- 120. Nakano, H., et al., *Effect of electrolysis factors on crystal orientation and morphology of electrodeposited cobalt.* Journal of Applied Electrochemistry, 2002. **32**(1): p. 43-48.
- 121. Vicenzo, A. and P. Cavallotti, *Growth modes of electrodeposited cobalt*. Electrochimica Acta, 2004. 49(24): p. 4079-4089.
- 122. Kılıç, F., et al., *Effect of CTAB concentration in the electrolyte on the tribological properties of nanoparticle SiC reinforced Ni metal matrix composite (MMC) coatings produced by electrodeposition*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013. **419**: p. 53-60.
- Beneaa, L., et al., *Preparation and investigation of nanostructured SiC–nickel layers* by electrodeposition. Solid State Ionics, 2002. 151(1-4): p. 89-95.
- 124. Heidari, G., H. Tavakoli, and S.M. Mousavi Khoie, Nano SiC-Nickel Composite Coatings from a Sulfamat Bath Using Direct Current and Pulsed Direct Current. Journal of Materials Engineering and Performance, 2010. 19(8): p. 1183-1188.
- 125. Ajaya Kumar Pradhan and S. Das, Pulse-reverse electrodeposition of Cu–SiC nanocomposite coating: Effect of concentration of SiC in the electrolyte. Journal of Alloys and Compounds, 2014. 590(25): p. 294-302.
- 126. Nakayama, A., et al., *Effect of Absorbed Hydrogen on Microstructure of Electrodeposited Cobalt.* ECS Transactions, 2010. **25**(34): p. 79-85.
- 127. Zanella, C., M. Lekka, and P. Bonora, *Effect of ultrasound vibration during electrodeposition of Ni–SiC nanocomposite coatings*. Surface Engineering, 2010.
 26(7): p. 511-518.
- 128. Zhao, K., et al., *Preparation and Properties of Nanocomposite Coatings by Pulsed Current-Jet Electrodeposition*. Int. J. Electrochem. Sci, 2017. **12**: p. 8578-8590.
- 129. Kanani, N., Electroplating: Basic Principles, Processes and Practice. 2004.
- Dehgahi, S., R. Amini, and M. Alizadeh, Corrosion, passivation and wear behaviors of electrodeposited Ni–Al2O3–SiC nano-composite coatings. Surface and Coatings Technology, 2016. 304: p. 502-511.
- Rudnik, E., Incorporation of ceramic particles into nickel and cobalt electroless deposits. Adv Mater Sci Appl, 2013. 2: p. 1-8.
- Addison, C. and E. Kedward, *The Development of Chromium Based Electrodeposited Composite Coatings*. Transactions of the IMF, 1977. 55(1): p. 41-46.
- Kumar, K., R. Chandramohan, and D. Kalyanaraman, *Effect of heat treatment on cobalt* and nickel electroplated surfaces with Cr2O3 dispersions. Applied surface science, 2004. 227(1-4): p. 383-386.

- 134. Rajiv, E., A. Iyer, and S. Seshadri, *Tribological properties of cobalt-partially stabilized zirconia (PSZ) composites in dry sliding conditions*. Wear, 1995. **189**(1-2): p. 100-106.
- 135. Rajiv, E. and S. Seshadri, *A study of the tribological properties of cobalt-titania composite*. Journal of materials science, 1993. **28**(7): p. 1758-1764.
- 136. Feng, Q., et al., Preparation and characterization of nickel nano-Al2O3 composite coatings by sediment co-deposition. Applied Surface Science, 2008. 254(8): p. 2262-2268.
- Shaffer, S. and M. Rogers, *Tribological performance of various coatings in unlubricated sliding for use in small arms action components—a case study.* Wear, 2007. 263(7-12): p. 1281-1290.
- Sangeetha, S., G.P. Kalaignan, and J.T. Anthuvan, *Pulse electrodeposition of self-lubricating Ni–W/PTFE nanocomposite coatings on mild steel surface*. Applied Surface Science, 2015. 359: p. 412-419.
- 139. Farzaneh, A., et al., *Electrochemical, structural and nano tribological behavior of Ni-W-PTFE nanocomposite coatings prepared by tartrate bath.* Int J Electrochem Sci, 2016. 11: p. 5140-5153.
- Bercot, P., E. Pena-Munoz, and J. Pagetti, *Electrolytic composite Ni–PTFE coatings:* an adaptation of Guglielmi's model for the phenomena of incorporation. Surface and Coatings Technology, 2002. 157(2-3): p. 282-289.
- 141. Iacovetta, D., J. Tam, and U. Erb, Synthesis, structure, and properties of superhydrophobic nickel–PTFE nanocomposite coatings made by electrodeposition.
 Surface and Coatings Technology, 2015. 279: p. 134-141.
- 142. Rezrazi, M., et al., *Au–PTFE composite coatings elaborated under ultrasonic stirring*.
 Surface and Coatings Technology, 2005. **192**(1): p. 124-130.
- Bushby, A. and D. Dunstan, *Plasticity size effects in nanoindentation*. Journal of materials research, 2004. **19**(1): p. 137-142.

- 144. Benea, L., P. Ponthiaux, and F. Wenger, Co-ZrO 2 electrodeposited composite coatings exhibiting improved micro hardness and corrosion behavior in simulating body fluid solution. Surface and Coatings Technology, 2011. 205(23): p. 5379-5386.
- 145. Wang, L., et al., A comparative study on the tribological behavior of nanocrystalline nickel and cobalt coatings correlated with grain size and phase structure. Materials Chemistry and Physics, 2006. 99(1): p. 96-103.
- 146. Leyland, A. and A. Matthews, On the significance of the H/E ratio in wear control: a nanocomposite coating approach to optimised tribological behaviour. Wear, 2000.
 246(1-2): p. 1-11.
- 147. Matthews, A. and A. Leyland. *Materials related aspects of nanostructured tribological coatings.* in 51st Annual Technical Conference Proceedings (Society of Vacuum *Coaters, Albuquerque, 2008).* 2009.
- 148. Mahdavi, S. and S. Allahkaram, *Characteristics of electrodeposited cobalt and titania nano-reinforced cobalt composite coatings*. Surface and Coatings Technology, 2013.
 232: p. 198-203.
- 149. Gyawali, G., et al., Effect of Ultrasonic Nanocrystal Surface Modification on Properties of Electrodeposited Ni and Ni-SiC Composite Coatings. Journal of Materials Engineering and Performance, 2017. 26(9): p. 4462-4469.

APPENDICES

Appendix I



I: Plug design to achieve consistency of all of the plating parameters in this work with the previous work[16]

								0					
Percent	at.%	SSD	Bath										
Тс	30s		40s		60s		90s		120s		DC		
Element													
Al	3.3	0.8	3.0	0.4	1.8	0.2	2.5	0.1	25	0.3	2.8	0.2	3a
Al^*	2.6	0.2	2.8	0.4	1.7	0.1	2.3	0.1	2.4	0.3	2.5	0.257	
0*	7.5	0.3	7.6	0.4	5.4	0.6	5.7	0.4	6.2	0.7	7.8	0.7	
Al	3.7	0.2	3.9	0.3	2.9	0.3	3.1	0.4	3.4	0.3	3.0	0.5	3b
Al^*	3.1	0.2	3.5	0.2	2.6	0.3	2.7	0.4	3	0.3	2.5	0.4	
O^*	8.9	0.7	9.8	0.9	7.6	1	7.9	1.3	9.9	0.7	8.5	1.0	
Al	5.0	0.9	4.1	0.4	3.2	0.4	3.4	1.2	3.0	0.4	2.8	0.4	3c
Al^*	3.6	0.4	3.5	0.7	2.4	0.3	2.5	0.8	2.6	0.3	2.5	0.4	
O^*	14.8	3.2	13.2	3.1	9.6	3.0	8.1	1.7	9.0	1.9	7.4	0.5	
Al	4.3	0.3	4.4	0.7	3.6	0.2	3.2	0.6	2.8	0.3	2.9	0.4	3d
Al^*	3.4	0.1	3.5	0.5	3.0	0.1	2.7	0.4	2.4	0.3	2.5	0.4	
O^*	11.0	1.3	10.9	0.8	9.0	0.4	9.2	1.0	8.2	0.6	8.5	0.2	
Al	3.8	0.4	4.4	0.3	3.7	0.4	2.7	0.4	3.0	0.3	2.7	0.3	3e
Al*	3.2	0.3	3.6	0.2	3.1	0.4	2.4	0.4	2.6	0.2	23	0.2	
<i>O</i> *	10.9	1.4	11.0	1.3	10.6	0.8	7.7	1.0	8.5	0.9	8.5	0.5	

Appendix 2: EDX analysis showing the chemical composition of coatings from bath 3 for Co-Al₂O₃

^{*} Symbols for each element represents the analysis done considering the oxygen in the coatings

P		· mousured	a deposited	111455 101 11	100011120	5 countrys	
Bath	tc(s)	30	40	60	90	120	DC
3a		84.7	108.8	132.1	153.7	165.2	166.7
<i>3b</i>		74.5	103.9	132.7	147.1	163.7	168.5
3c		78.8	107.5	135	153.1	161.9	167.5
3d		82.5	105.1	132.9	152.1	159.3	166.9
3e		77.5	105.7	130.2	152	161.5	165.6

Appendix 3: Measured deposited mass for the Co-Al₂O₃ coatings

Appendix 4: Calculating deposited mass of co and nano al₂O₃ particles and cathodic current efficiency from the coatings thickness

Bath	tc	Cycles	th	Al ₂ O ₃	tth	tth mCo,dep		ot	t _{Co} per cycle	
	[s]	incl.		[µm]	[vol.%]	[µm]	[mg]	[%]	[µm]	
3a	30	43	120	24.5	6.3	27.1	82	93.5	0.191	
	40	57	90	26.2	5.7	32.3	106	90.4	0.274	
	60	71	60	31.5	3.5	37.8	130	88.7	0.507	
	90	81	40	31.9	4.7	44.3	150	90.5	0.760	
	120	86	30	31.8	4.8	47.7	162	91.9	1.008	
	DC	100	1	36.6	5.3	48.2	163	92.5	34.705	
3b	30	43	120	24.5	6.9	23.2	72	82.0	0.190	
	40	57	90	27.8	7.2	31.3	100	85.6	0.287	
	60	71	60	32.0	5.4	38.4	129	88.3	0.504	
	90	81	40	37.0	5.9	42.7	143	86.2	0.871	
	120	86	30	39.0	6.4	47.7	159	90.3	1.216	
	DC	100	1	31.8	5.6	48.9	164	93.3	29.986	
3c	30	43	120	27.7	9.2	24.5	75	85.7	0.210	
	40	57	90	26.9	7.7	32.9	104	88.4	0.276	
	60	71	60	30.7	6.1	39.2	131	89.5	0.480	
	90	81	40	36.2	6.3	44.6	149	89.5	0.848	
	120	86	30	36.5	5.6	46.9	158	89.7	1.148	
	DC	100	1	38.9	5.3	48.5	163	92.9	36.814	
3d	30	43	120	29.1	8.0	28.7	79	90.3	0.223	
	40	57	90	30.1	8.1	31.4	101	86.2	0.308	
	60	71	60	34.1	6.8	38.8	129	87.8	0.530	
	90	81	40	33.4	5.9	44.2	148	89.1	0.785	
	120	86	30	36.4	5.2	46.1	156	88.4	1.149	
2	DC	100	1	35.9	5.5	48.4	163	92.5	33.896	
3e	30	43	120	24.9	7.1	23.8	75	85.2	0.193	
	40	57	90	28.0	8.2	34.7	102	86.7	0.285	
	60	71	60	34.1	7.0	38.4	126	85.9	0.529	
	90	81	40	32.0	5.2	45.8	148	89.3	0.758	
	120	86	30	38.5	5.6	46.8	157	89.5	1.211	
	DC	100	1	36.6	5.2	47.9	162	91.9	34.694	