



UNIVERSITI PUTRA MALAYSIA

***SYNTHESIS AND CHARACTERIZATION OF Ni-Al₂O₃-Cr, Ni-Al₂O₃-SiC
AND Ni-SiC-Cr NANO HYBRID COMPOSITES***

MEHRAN MASOUDI

FS 2013 4

**SYNTHESIS AND CHARACTERIZATION OF
Ni-Al₂O₃-Cr, Ni-Al₂O₃-SiC AND Ni-SiC-Cr NANO
HYBRID COMPOSITES**

The logo of Universiti Putra Malaysia (UPM) is a shield-shaped emblem. It features a red and white design with a central vertical element and a book at the top. The letters 'UPM' are prominently displayed in a red box at the top left of the shield.

MEHRAN MASOUDI

DOCTOR OF PHILOSOPHY

UNIVERSITI PUTRA MALAYSIA

2013

**SYNTHESIS AND CHARACTERIZATION OF Ni-Al₂O₃-Cr, Ni-Al₂O₃-SiC
AND Ni-SiC-Cr NANO HYBRID COMPOSITES**

By

MEHRAN MASOUDI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

January 2013

Abstract of thesis presented to the Senate of Universiti Putra Malaysia, in fulfillment
of the requirement for the degree of Doctor of Philosophy

**SYNTHESIS AND CHARACTERIZATION OF Ni-Al₂O₃-Cr, Ni-Al₂O₃-SiC
AND Ni-SiC-Cr NANO HYBRID COMPOSITES**

By

MEHRAN MASOUDI

January 2013

Chairman: Associate Professor. Mansor Hashim, PhD

Faculty: Science

This research is focused on the preparation of nickel base composites having nano particles of chromium, alumina and silicon carbide in the form of mono and hybrid composites by using a co-electrodeposition technique in nano powders of SiC, Cr, and Al₂O₃ with a 50 nm mean dimension were introduced into the conventional nickel plating Watt's bath. The prepared new hybrid composites, mono nickel based composites and pure nickel layers were subjected to different tests to characterize their surface morphology, crystalline structure, mechanical properties and hot oxidation resistance. The microstructure and composition of the composite films were studied with field emission scanning electron microscopy (FE-SEM), XRD spectroscopy and EDS techniques. Micro hardness and wear tests were carried out on coated samples to investigate the mechanical properties.

The test results showed effectiveness and flexibility of the co-electrodeposition technique in creating mono and more complicated nickel base composite layers. The novel Ni-Al₂O₃-Cr composite layer showed considerable improvement in hot oxidation resistance compared to the pure nickel layer and the Ni-Al₂O₃ composite; and it enhanced mechanical properties compared to Ni and Ni-Cr composite films. This newly created hybrid composite could be a good substitution for commercial Ni-Al₂O₃ and Ni-Cr composites.

The fabricated novel Ni-Al₂O₃-SiC composite film showed superior mechanical properties among all the mono and hybrid composites studied in this research; and, by comparison with the Ni-Al₂O₃ composite, exhibited enhanced hot oxidation resistance. Its high hardness and wear resistance along with acceptable thermal stability makes the Ni-Al₂O₃-SiC composite film a good choice for coating many industrial parts and components as an anti-oxidation and anti-wear protective film.

The newly fabricated Ni-SiC-Cr nanocomposite coating displayed the highest hot oxidation resistance among all the tested composites in this study owing to chromium's excellent corrosion and oxidation resistant properties. Advantageously, it formed silicon oxide that reduced the diffusion rate at elevated temperatures. The SiC hard and anti-wear particles rendered good mechanical properties to the synthesized hybrid composite. The altered surface morphology, fine crystalline structure, advanced oxidation resistance and improved mechanical properties enable Ni-SiC-Cr composite films to protect metallic parts in high severe corrosive, abrasive and thermal working conditions.

A quantitative technique for measuring grain boundary volume percentage using XRD test results have been suggested and tested successfully in this thesis. This

technique could be a reliable base for future fundamental studies on nano materials deformation mechanisms.

The achievements of the project work laid out in detail in this thesis can be summarized in the following points:

- Successful co-electrodeposition of the Ni- Al_2O_3 , Ni-SiC and Ni-Cr mono composites by an electroplating technique.
- Preparation of novel Ni- Al_2O_3 -Cr hybrid nanocomposite coatings with excellent mechanical properties, improved anti-oxidation by 55% and attribute advanced thermal resistance.
- Preparation of novel Ni- Al_2O_3 -SiC hybrid nanocomposite coatings with superior mechanical properties (three times harder than pure nickel film) and improved hot oxidation resistance.
- Preparation of novel Ni-SiC-Cr hybrid nanocomposite coatings having superior hot oxidation resistance (90% better than pure nickel film) and improved mechanical properties especially wear resistant behaviour.
- Detailed study and discussion on the surface morphology, crystalline structure and texture of the created mono and hybrid composite layers.
- Detailed study comparative on mechanical characterizations of a pure nickel film and mono as well as hybrid composite coatings.
- Detailed study on the oxidation kinetics of prepared MMC coated samples having different varieties in the form of Cr, SiC and Al_2O_3 filler substances.
- Formulation of a new quantitative technique for measuring the grain boundary volume percentage in polycrystalline materials.

Abstrak Tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN KOMPOSIT HIBRID NANO Ni-Al₂O₃-Cr, Ni-Al₂O₃-SiC DAN NI-SiC-Cr

Oleh

MEHRAN MASOUDI

January 2013

Pengerusi : Associate Professor Mansor Hashim, PhD

Fakulti : Sains

Fokus tesis ini adalah mengenai penyediaan komposit asas nikel yang mempunyai partikel nano kromium, alumina dan silikon karbida dalam bentuk komposit mono dan komposit hibrid dengan menggunakan teknik pemendapan elektro bersama elektro. Serbuk nano SiC, Cr, dan Al₂O₃ dengan min dimensi 50 nm telah diperkenalkan kepada saduran nikel secara konvensional iaitu Watt's bath. Komposit hibrid baru yang telah disediakan, komposit berasaskan nikel mono dan lapisan nikel tulen telah melalui ujian yang berbeza untuk mengenalpasti ciri-ciri morfologi permukaan, struktur hablur, sifat mekanik dan rintangan pengoksidaan panas masing-masing. Mikrostruktur dan komposisi komposit filem telah dikaji dengan pancaran mikroskopi elektron imbasan (FE-SEM), spektroskopi XRD dan teknik EDS. Ujian kekerasan mikro dan ujian kehausan telah dijalankan ke atas sampel bersalut untuk menyiasat sifat-sifat mekanik.

Keputusan ujian menunjukkan keberkesanan dan fleksibiliti teknik pemendapan elektro bersama dalam mewujudkan lapisan komposit mono dan lapisan komposit berasaskan nikel yang lebih rumit. Lapisan komposit Ni-Al₂O₃-Cr yang baru menunjukkan peningkatan rintangan pengoksidaan panas berbanding dengan lapisan nikel tulen dan Ni-Al₂O₃ malah sifat-sifat mekanik komposit telah dipertingkatkan berbanding komposit filem Ni dan Ni-Cr. Komposit hibrid yang diperkenalkan ini boleh menjadi pengganti baik untuk komposit Ni-Al₂O₃ dan Ni-Cr komersial.

Fabrikasi komposit filem Ni-Al₂O₃-SiC yang baru menunjukkan sifat-sifat mekanik unggul antara semua mono dan deposit hibrid yang telah dikaji dalam penyelidikan ini dan dalam perbandingan dengan komposit Ni-Al₂O₃, menggambarkan peningkatan rintangan terhadap pengoksidaan panas. Komposit filem Ni-Al₂O₃-SiC dengan kekerasan dan rintangan haus yang tinggi bersama-sama dengan kestabilan terma yang bersesuaian membuatkan Ni-Al₂O₃-SiC menjadi pilihan komposit filem yang baik untuk saduran banyak bahagian dan komponen industri sebagai lapisan anti pengoksidaan dan lapisan pelindung anti-kehausan.

Fabrikasi baru salutan komposit nano Ni-SiC-Cr menunjukkan rintangan pengoksidaan panas tertinggi antara semua komposit yang diuji dalam kajian ini disebabkan oleh tahap tahan kakisan kromium yang sangat baik dan sifat tahan pengoksidaan serta peranan silikon oksida yang terbentuk dalam mengurangkan kadar resapan pada suhu tinggi. Partikel keras dan anti-haus SiC memberikan sifat-sifat mekanik yang baik kepada komposit hibrid disintesis ini. Morfologi permukaan yang telah berubah, struktur kristal yang halus, rintangan pengoksidaan yang ditingkatkan dan sifat-sifat mekanik yang bertambah baik membolehkan komposit filem Ni-SiC-Cr melindungi bahagian-bahagian logam ketika berada dalam keadaan pengakisan, penglelasan dan kerja panas yang teruk.

Teknik kuantitatif bagi mengukur jumlah peratusan isipadu sempadan butiran menggunakan keputusan ujian XRD telah dicadangkan dan diuji dengan jayanya dalam tesis ini. Teknik ini boleh menjadi asas yang boleh dipercayai untuk kajian asas mekanisme canggaan bahan nano.

Pencapaian kerja projek yang dibentangkan secara terperinci dalam tesis ini boleh diringkaskan melalui perkara-perkara berikut:

- Kejayaan pemendapan elektro bersama komposit mono Ni-Al₂O₃, Ni-SiC dan Ni-Cr melalui teknik penyaduran elektro.
- Penyediaan salutan komposit nano hibrid Ni-Al₂O₃-Cr baru dengan sifat mekanikal yang diperbaiki, sifat anti-pengoksidaan yang lebih baik dan rintangan haba yang meningkat sebanyak 50%.
- Penyediaan salutan komposit nano hibrid Ni-Al₂O₃-SiC baru dengan sifat mekanikal unggul (tiga kali lebih kuat daripada filem nikel tulen) dan rintangan pengoksidaan panas yang lebih baik.
- Penyediaan salutan komposit nano hibrid Ni-SiC-Cr baru g mempunyai rintangan pengoksidaan panas yang mantap (90% lebih baik daripada saduran nikel tulen) dan sifat-sifat mekanik yang bertambah baik terutama ciri kehausan.
- Kajian terperinci dan perbincangan morfologi permukaan, struktur kristal dan tekstur mono yang telah dihasilkan serta lapisan komposit hibrid.
- Kajian perbandingan terperinci ciri mekanikal filem nikel tulen, serta salutan komposit mono dan hibrid secara perbandingan.
- Mengkaji kinetik pengoksidaan sampel bersalut MMC yang disediakan dengan pelbagai bahan pengisi Cr, SiC dan Al₂O₃ yang berbeza.
- Penghasilan teknik kuantitatif baru bagi mengukur jumlah peratusan isipadu sempadan butiran dalam bahan polihablur.

AKNOWLEDGEMENTS

It would not have been possible to write this doctoral thesis without the help and support of the kind people around me, to only some of whom it is possible to give particular mention here. I would never have been able to finish my dissertation without the guidance of my committee members, help from friends, and support from my family and wife.

Above all, I would like to express my appreciation to my principle supervisor Associate Prof Dr. Mansor Hashim for his excellent guidance, caring, patience, and providing me with an excellent atmosphere which were always a strong support during my studies. I am highly indebted and extremely grateful. The good advice, support and friendship of my supervision committee, Professor Dr. Mohd Sapuan Salit and Dr. Halimah Mohamed Kamari have been invaluable on both an academic and a personal level, for which I am extremely grateful.

I would like to thank my wife Shohreh and my daughters Kiana and Romina for their personal support and great patience at all times. My parents have given me their unequivocal support throughout, as always, for which my mere expression of thanks likewise does not suffice. They were always supporting me and encouraging me with their best wishes.

Lastly and most importantly, I wish to thank my colleagues who become my best friends in the magnetic materials research group. I am pleased about your hospitality, opinions and highly support and it was an honour to work and be with you all.

APPROVAL

I certify that a Thesis Examination Committee has met on ----- to conduct the final examination of Mehran Masoudi on his PhD thesis entitled “**Synthesis and Characterization of Ni-Al₂O₃-Cr, Ni-Al₂O₃-SiC and Ni-SiC-Cr Nano Hybrid Composites**” in accordance with the Universities AND University Colleagues Act 1971 and the Constitution of the Universiti [P.U.(A)106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy degree.

Members of the Thesis Examination Committee were as follows:

Chairperson, PhD

Professor

Name of Faculty

Universiti Putra Malaysia

(Chairperson)

Name of Examiner 1, PhD

Professor

Name of Faculty

Universiti Putra Malaysia

(Internal Examiner)

Name of Examiner 2, PhD,

Professor

Name of Faculty

Universiti Putra Malaysia

(Internal Examiner)

External Examiner, PhD

Professor

Name of Faculty

Name of Organization

(External Examiner)

BHJANG KIM HAUT, PhD.

Professor and Deputy Dean

School of Graduate Studies

Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Mansor Hashim, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Sapuan Salit, PhD, IR

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Halimah Mohd Camari, PhD

Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, Ph.D.

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

MEHRAN MASOUDI

Date: 10st January 2013

TABLE OF CONTENTS

	Page
ABSTRACT	iii
ABSTRAK	vi
AKNOWLEDGEMENTS	ix
APPROVAL	x
DECLARATION	xii
LIST OF TABLES	xviii
LIST OF FIGURES	xx
LIST OF ABBREVIATIONS	xxvi
CHAPTER	
I	
INTRODUCTION	1
1.1	1
Background of Study	
1.2	2
Motivation for the Present Study	
1.3	4
Market Opportunities	
1.4	5
Problem Statement	
1.5	6
Objectives of the Research Work	
1.6	7
Thesis Outline	
II	
LITERATURE REVIEW	9
2.1	9
Properties of Nickel and its Applications	
2.1.1	10
Nickel Oxidation Resistance	
2.1.2	12
Wear Resistance Alloys	
2.2	12
Nickel Electroplating	
2.2.1	14
Watt's Nickel Plating Solution	
2.2.2	15
Nickel Sulphamate Solution	
2.2.3	15
All-Chloride Solution	
2.2.4	16
Sulphate-Chloride Solution	
2.2.5	17
Fluoborate Solution	
2.2.6	18
All-Sulphate Solution	
2.2.7	18
Hard Nickel Solution	

2.2.8	Anodes	19
2.2.9	Current Efficiency	19
2.2.10	Surface Preparation	20
2.2.11	Problems	21
2.3	Improving Nickel Layer Properties	22
2.4	Metal Matrix Composite (MMC)	26
2.4.1	MMC Mechanical Properties	27
2.4.2	MMC Corrosion Resistance	32
2.4.3	MMC Hot Oxidation Resistance	33
2.5	A Review of Nickel Matrix Composites	36
2.5.1	Ni – Cr Composite	37
2.5.2	Ni- CeO ₂ Composite	41
2.5.3	Ni-PTFE Composite	42
2.5.4	Ni- SiC Composite	44
2.5.5	Ni- SiO ₂ Composite	46
2.5.6	Ni- TiO ₂ Composite	47
2.5.7	Ni-Al Composite	49
2.5.8	Ni- Al ₂ O ₃ Composite	51
2.5.9	Ni-La ₂ O ₃ Composite	56
2.5.10	Ni-ZrO ₂ Composite	57
2.5.11	Ni-Y ₂ O ₃ Composite	59
2.5.12	Ni-W Composite	60
2.5.13	Ni-Al-SiC Composite	61
2.5.14	Ni-Al-Cr Composite	61
2.5.15	Ni/Cr- Al ₂ O ₃ Composite	63
2.5.16	Ni-Cu-P-PTFE Composite	64
2.5.17	Ni- Al-Y ₂ O ₃ Composite	64
2.5.18	Ni-Co-Mo ₂ S Composite	66
2.5.19	Ni-Co/ Al ₂ O ₃ Composite	67
2.5.20	Ni-W-P /CeO ₂ -SiO ₂ Composites	68
2.5.21	Ni-Co/Nano Carbon Tube Composite	68
2.6	Manufacturing Technologies and Challenges	69

III	THEORY	71
3.1	Introduction	71
3.2	Faraday's Law	71
3.3	Diffusion	74
3.4	Oxidation	77
3.5	Fine Grain Structure	83
3.5.1	Grain Size and Strength	86
3.5.2	Grain Size Determination Techniques	88
3.5.3	Process Parameters	92
3.5.4	Particle Sizes	93
3.5.5	Plating Direction – Gravity Effect	95
3.5.6	Optimum Filler Concentration in the Electrolyte	96
3.5.7	Powder Deposition Rate	99
3.5.8	Additives	100
3.5.9	Aging	102
3.5.10	Agitation Effect	103
3.5.11	Temperature	104
3.5.12	Bath Composition	105
3.5.13	pH	106
3.5.14	Current Density	108
IV	METHODOLOGY	111
4.1	Introduction	111
4.2	Experiment Design	112
4.3	Materials	118
4.4	Sample Preparation	119
4.5	Set up for the Electroplating cell	120
4.6	Oxidation Test	123
4.7	Materials Characterization Techniques	124
4.7.1	X-ray Diffraction (XRD)	125
4.7.2	Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX) Spectroscopy	128
4.7.3	Hardness Test	132

4.7.4	Wear Resistance	134
V	RESULTS AND DISCUSSION	135
5.1	Introduction	135
5.2	Co-Electrodeposition of Nickel and Nickel Mono Composite Films	136
5.2.1	Nickel Electroplating	138
5.2.2	Ni-Cr Nanocomposite Coatings	148
5.2.3	Ni-SiC Composite Coating	158
5.2.4	Ni-Al ₂ O ₃ Composite Coating	166
5.3	Comparison of Mono Ni-Al ₂ O ₃ , SiC and Cr Nanocomposites Properties	175
5.3.1	Crystalline Structure	176
5.3.2	Texture	177
5.3.3	Surface Morphology	179
5.3.4	Nickel Matrix Grain Sizes	180
5.3.5	Deposition Rate	182
5.3.6	Agglomeration	184
5.3.7	Mechanical Properties	185
5.4	Nickel Based Hybrid Composites	194
5.4.1	Ni-Al ₂ O ₃ -Cr Hybrid Composite Coating and Characterization	195
5.4.2	Ni-SiC-Cr Hybrid Composite Coating and Characterization	210
5.4.3	Ni-Al ₂ O ₃ -SiC Hybrid Composite Coating and Characterization	222
5.5	Hot Oxidation Resistance	236
5.5.1	Introduction	236
5.5.2	Experimental Details in Brief	238
5.5.3	Oxide Layer Morphology and Crystalline Structure	240
5.5.4	Kinetics of Oxidizing	243
5.6	The Grain Boundary Quantitative Study	256
5.6.1	Introduction	256

5.6.2	Experimental Details in Brief	258
5.6.3	Quantitative and Qualitative Analysis	259
5.6.4	Advantages and Disadvantages	264
5.6.5	Summary	264
VI	CONCLUSIONS AND SUGGESTIONS	266
6.1	Conclusions	266
6.2	Suggestions for Further Works	269
	REFERENCES	271
	APPENDICES	280
A	Nickel Physical, Chemical and Atomic Properties	280
B	Hardness Conversion Table	282
	BIODATA OF THE AUTHOR	284
	LIST OF PUBLICATIONS	285