Faculty of Manufacturing Engineering

TRIBOLOGICAL AND ELECTROCHEMICAL BEHAVIOR OF ELECTROLESS QUATERNARY NICKEL ALLOY DEPOSITION FOR CUTTING TOOLS

Mohamad Noor Azran bin Mohamad Noor

Master of Science in Manufacturing Engineering

2018

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MOHAMAD NOOR AZRAN BIN MOHAMAD NOOR

A thesis submitted
in fulfillment of the requirements for the degree of Master of Science
in Manufacturing Engineering

Faculty of Manufacturing Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2018

DECLARATION

I declare that this thesis entitled "Tribological and Electrochemical Behavior of Electroless Quaternary Nickel Alloy Deposition for Cutting Tools" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : .....

Name : .....

Date : .....

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering.

Signature	:	……...
Supervisor Name	:	……
Date	:	……

DEDICATION

To my beloved mother Mardziah Binti Mustafa, father Mohamad Noor Bin Jusoh and family who taught me that even the largest task can be accomplished if it is done one step at a time.

ABSTRACT

Coating on steel can improve various characteristics such as corrosion resistance in salt water, surface hardness and wear resistance. One of the coating methods is electroless deposition using reducing agent to reduce metal ion onto substrate. Electroless nickel deposition using hypophosphite as reducing agent can produce a binany Ni-P alloy that has superior properties than Ni itself. Furthermore, the formation of quaternary Ni alloy can be produced by adding other metal ions such as Co, Cu, Zn, and W. The addition of Cu in the Ni-P alloy matrix improves the corrosion resistance in salt water by increasing its barrier resistance and also surface properties. Co addition provides the passive film formation while retaining the corrosion potential in salt water at noble potential compare to steel. However, the effect of Cu and Co ions addition in hypophosphite based electroless Ni bath on its quaternary Ni alloy formation, mechanism and its properties is still less known. In this work, electroless Ni-Co-Cu-P alloy deposit on steel was produced using hypophosphite base electroless Ni plating bath by adding cobalt and copper salts into the plating bath solutions. The effect of cobalt and copper addition on the surface morphology, hardness, and elemental composition of nickel alloy deposition rate was investigated via analysis with a Scanning Electron Microscope (SEM), microVickers Hardness Tester and X-ray Fluorescence (XRF) respectively. Coefficient of friction and wear rate of the coating was studied and analyzed using Pin-on-Disk test. Corrosion behavior of electroless quaternary Ni alloy deposit was studied using polarization curve measurements in a classical three electrode configuration using the coating surface as a working electrode, graphite as a counter electrode and Ag/AgCl/KCl(saturated) as a reference electrode. Besides that, the reaction mechanism is analyzed using cyclic voltammetry measurement using graphite as both counter and working electrode.The electroless quaternary Ni alloy with Cu, Co and P alloying element has been suscessfully done in both alkaline and acidic bath. The Co is easily deposited in alkaline bath while Cu in acidic bath based on XRF result. The corrosion behavior of Ni-Co-Cu-P from pH 9.5 bath has the most excellent corrosion resistance behavior in salt solution that is 14.21 mm per year due to more noble corrosion potential and passive film potential compare to Ni-Cu-Co-P alloy and steel. Highest Co content in the Ni-Co-Cu-P alloy that is 5.79 wt% exhibit the highest hardness 991.3 HV compare to other Ni alloy compositions as well as Ni-W-P alloy. Nevertheless, the coefficient friction of the quaternary Ni alloy with higher Cu content (Ni-Cu-Co-P) is lower that Ni-Co-Cu-P alloy.

ABSTRAK

Salutan pada keluli boleh meningkatkan pelbagai ciri seperti ketahanan kakisan dalam air garam, kekerasan permukaan dan ketahanan hausan. Salah satu kaedah salutan adalah pemendapan penyaduran tanpa elektrik menggunakan ejen penurunan untuk menurunkan ion logam ke atas substrat. Pemendapan nikel tanpa elektrik menggunakan hipofospit sebagai agen penurunan boleh menghasilkan aloi Ni-P yang mempunyai sifat lebih bagus daripada Ni itu sendiri. Selain itu, pembentukan aloi kuaternerari boleh dihasilkan dengan menambah ion logam lain seperti Co, Cu, Zn, dan W. Penambahan Cu dalam matriks aloi Ni-P meningkatkan rintangan kakisan dalam air garam dengan meningkatkan rintangan penghalang dan juga sifat-sifat permukaan. Penambahan Co menyediakan pembentukan filem pasif sambil mengekalkan potensi kakisan dalam air garam pada potensi positif berbanding dengan keluli. Walaubagaimanapun, kesan penambahan ion Cu dan Co dalam di dalam bancuhan larutan Ni-hipofosphit untuk penyaduran tanpa elektrik kepada pembentukan aloi kuaternari Ni, mekanisma dan sifatnya masih kurang diketahui. Dalam penyelidikan ini, deposit aloi kuaternari Ni ke atas keluli dihasilkan menggunakan penyaduran tanpa elektrik di dalam bancuhan Ni-hipofosfit dengan menambah garam kobalt dan kumprum ke dalam larutan bancuhan untuk penyaduran tanpa elektrik. Kesan tambahan kobalt dan kuprum pada morfologi permukaan, kekerasan dan komposisi unsur dan kadar pemendapan aloi nikel diselidiki melalui analisis dengan Mikroskop Pengimbasan Elektron (SEM), Penguji Kekerasan MikroVickers dan analisis Pendafluor X-Ray (XRF). Geseran pekali dan kadar kehausan saduran dikaji dan dianalisis menggunakan ujian "Pin-on-Disk". Sifat kakisan saduran tanpa elektrik aloi kuaternari Ni aloi telah dikaji menggunakan pengukuran lengkung polarisasi (LSV) menggunakan konfigurasi klasik tiga elektrod menggunakan permukaan salutan sebagai elektrod bekerja, grafit sebagai elektrod berbalas dan Ag/AgCl/KCl(tepu) sebagai elektrod rujukan. Selain itu, mekanisma tindak balas dianalisis dengan menggunakan pengukuran kitaran voltammetr yang menggunakan grafit sebagai elektrod berbalas dan elektrod bekerja. Saduran tanpa electrik aloi kuaternari Ni dengan unsur Cu, Co dan P telah dilakukan secara perlahan-lahan dalam larutan alkali dan juga larutan berasid. Co mudah disadur di dalam larutan alkali manakala Cu dalam larutan asid berdasarkan hasil analisis XRF. Sifat kakisan Ni-Co-Cu-P dari larutan pH 9.5 mempunyai sifat tahan kakisan yang paling baik dalam larutan garam iaitu 14.21 mm kerana potensi karat yang lebih tinggi dan pembentukan filem pasif berbanding dengan aloi Ni-Cu-Co-P dan keluli. Kandungan Co tertinggi dalam aloi Ni-Co-Cu-P iaitu 5.79 wt% menunjukkan kekerasan tertinggi 991.3 HV berbanding komposisi aloi Ni yang lain termasuk Ni-W-P. Walaubagaimanapun, geseran pekali aloi kuarternari Ni yang mempunyai kandungan Cu yang lebih tinggi (Ni-Cu-Co-P) adalah lebih rendah daripada aloi Ni-Co-Cu-P.

ACKNOWLEDGEMENTS

First and foremost, I would like to take this opportunity to express my sincere acknowledgement to my supervisor Dr. Muhammad Zaimi Bin Zainal Abidin from the Faculty of Manufacturing Engineering Universiti Teknikal Malaysia Melaka (UTeM) for his essential supervision, support and encouragement towards the completion of this thesis and also my co-supervisor Dr. Mohd Shahir Bin Kasim.

I would also like to express my greatest gratitude to UTeM short term grant funding PJP/2013/FKP(6A)/S01180 and Ministry of Higher Education for RAGS grant RAGS/2013/FKP/TK04/01//B00028, for the financial support throughout this project. Special thanks to Zuraida Binti Hamzah, Muhammad Alif Bin Abd Aziz and Muhamad Khaizaki Bin Ahmad for their laboratory work.

Special thanks also to all my colleagues, my beloved mother, father and siblings for their moral support in completing this degree. Lastly, thank you to everyone who had been associated to the crucial parts of realization of this project. Not forgetting, my humble apology as it is beyond my reach personally mentioned those who are involved directly or indirectly one to one.

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LIST OF ABBREVIATIONS

CBD	-	Chemical Bath Deposition
CV	-	Cyclic Voltammetry
CVD	-	Chemical Vapor Deposition
EN	-	Electroless Nickel
EW	-	Equivalent Weight
HV	-	Hardness Vickers
Mpy	-	Mili-inches per Year
PVD	-	Physical Vapor Deposition
Redox	-	Reduction Potential
Rpm	-	Round per Minutes
SEM	-	Scanning Electron Microscope
XRD	-	X-ray Diffraction
XRF	-	X-ray Fluorescence

LIST OF SYMBOLS

Co	-	Cobalt
Cu	-	Copper
Co-P	-	Cobalt-Phosphorus
Cu-P	-	Copper-Phosphorus
Ecorr	-	Corrosion Potential
H^+	-	Hydrogen Ions
HCl	-	Hydrochloric Acid
Icorr	-	Corrosion Current Density
M	-	Mol
Mm	-	Milimeter
Ni^{2+}	-	Nickel Ions
NaCl	-	Sodium Chloride
NaOH	-	Sodium Hydroxide
Ni-P	-	Nickel-Phosphorus
Ni-Co-P	-	Nickel-Cobalt-Phosphorus
Ni-Cu-P	-	Nickel-Copper-Phosphorus
Ni-W-P	-	Nickel-Tungsten-Phosphorus
Ni-Co-Cu-P	-	Nickel-Cobalt-Copper-Phosphorus
P	-	Phosphorus

Sn	-	Tin
W	-	Tungsten
Zn	-	Zinc
M	-	Micron
^{o}c	-	Degree Celcius
%	-	Percent
D	-	Density

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Electroless nickel alloy deposition is widely used as a coating in the industry due to their excellent properties such as corrosion resistance and hardness. Compare to Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) coating. Electroless nickel alloy deposition produces uniform coating on any shape and type of substrate. Other than that, it does not need external current supply to produce coating and less porous deposited compared to electroplating. In electroless nickel alloy deposition bath, the reducing agent such as hypophosphite is to reduce the nickel ion into metallic nickel onto the substrate producing a binary Ni-P alloy. The Ni-P alloy is widely used in various industries such as chemical and electronic industry because of their excellent properties which depend on the phosphorus content. According to Balaraju et al., (2005), the presence of phosphorus in binary Ni-P alloy improves the properties of the metal to be plated such as corrosion and wear resistance, hardness, magnetic properties and electrical resistance.

Furthermore, the properties of Ni-P alloy is been such as corrosion resistance and hardness can been improved by developing ternary electroless nickel alloy with addition of another metallic element such as copper, cobalt, tungsten, molybdenum and becoming Ni-Cu-P, Ni-Co-P, Ni-W-P, and Ni-Mo-P alloy respectively. The inclusion of copper in Ni-P matrix has enhances the deposit characteristic such as

corrosion resistance, brightness, and ductility (Balaraju et al., 2005). Other than that, the additions of tungsten in binary Ni-P alloy can improve the properties of the coating such as electrical resistance and thermal stability (Balaraju et al., 2005). The operating parameter such as pH, temperature and metal ion concentration give significant effect to the metal additive content in electroless ternary nickel alloy. The deposition rate is increases and phosphorus content is decreased as increasing bath. The previous study of electroless Ni-Co-P by Aly et al., (2003) shows that the cobalt content increase as increasing in pH, temperature and copper sulphate concentration but decrease the phosphorus content.

Other than ternary nickel alloy, quaternary nickel alloy is developed with the addition of another element as a fourth element for the purpose of further improvement properties such in corrosion and surface morphology. There are several quaternary nickel alloys that reported being produced using electroless methods such as Ni-W-Cu-P, Ni-Re-W-P, Ni-Mo-Cr-P, Ni-Fe-P-B, Ni-W-Cr-P, Ni-Zn-Cu-P and Ni-W-Sn-P. The previous study from Balaraju et al., (2005) proved that ternary Ni-W-P deposits are coarse whereas quaternary Ni-Cu-W-P deposits are smooth, nodule-free and quaternary nickel alloy increase the crystallinity of the alloy which also improved the corrosion resistance of the coating. The addition of copper and tungsten additive in Ni-P has improved the corrosion properties of the deposit. However, the corrosion resistance of electroless Ni-Zn-Cu-P alloy is the lowest compared with Ni-P, Ni-Zn-P and Ni-Cu-P alloy (Zaimi et al., 2013). The effect of zinc and copper addition produce a lowest corrosion while the effect of tungsten and copper addition produce excellent corrosion resistance. The effect of copper and cobalt additive in Ni-P matrix on its corrosion is still less known.