Electrodeposition of Compositionally Modulated Alloys – An Overview

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SUMMARY – A new class of materials known as compositionally modulated alloys (CMA) or artifici modulated multilayers has generated an ever-increasing enthusiasm due to their unique properties. T paper reviews the recent developments in the field of electrodeposition techniques for the production CMA, which offers many advantages over other methods. It also discusses the structure of CMA and th salient properties such as corrosion resistance, magnetic and mechanical properties, which differ to th obtainable in normal metallurgical alloys. Some of their interesting applications are also discussed.

Keywords: Electrodeposition, CMA, Multilayers.

INTRODUCTION

A new class of materials with alternating layers of different metals having thickness of few nanometers with ultra fine microstructure known as Compositionally Modulated Alloys (CMA)[1] or Compositionally Modulated Multilayers (CMM) have been developed. As a result of layering at atomic dimensions, they exhibit unusual and outstanding properties such as enhanced mechanical, magnetic properties etc, which are not obtainable in normal metallurgical alloys. CMM are also being used as ideal model systems in the study of fundamental aspects of materials in the field of magnetism, electrical transport phenomenon and thermodynamic properties etc.

There are two methods of obtaining modulated alloys, (i) physical (PVD) and (ii) chemical (CVD, Electrodeposition). Physical methods include PVD, evaporation, sputtering and molecular beam epitaxy techniques. Many different systems[2-3] have been prepared by PVD such as Si/Nb and Co/X where X is either Au or Pd or Cu. The above methods have several advantages for specific applications, but due to some limitations of above methods such as high capital cost, high-energy cost etc, an alternative method is required. Electrolytic deposition has fulfilled this need. This paper discusses the electrodeposition technique, its relative merits over the other methods, types of bath, experimental parameters, characterisation of some CMA systems by SEM, AFS, XRD analysis, their properties such as tensile strength, micro hardness, magnetic properties etc, and the various industrial applications.

ELECTRODEPOSITION

The electrodeposition technique has aroused a great deal of interest. Blum[4] first introduced the electrodeposition of multilayered alloy on Cu-Ni in the 1920s. Later on Brenner[5] deposited Cu/Bi by varying current density. Electrodeposition offers certain advantages over the other conventional methods. It is a cheap and well-established industrial process and is a precisely, controlled room temperature operation. Thus, the risk of interdiffusion is low and the deposition rate is fast with low energy requirements. Binary, ternary and quaternary alloys over a wide range of composition, and structures are easily obtainable by this technique. Electrodeposition has wide applications in various industries including those of the aircraft, aerospace, automotive, household appliances and electronics. Electrodeposition of CMA can be carried out in two major ways, namely (i) the Single bath technique and (ii) the Dual bath technique.

Single Bath Technique

The single bath technique is where a pure metal and an alloy of the first metal are plated successively by changing the current density, by controlling diffusion near the cathode surface, by changing the agitation or by a combination of these parameters. Moreover, the single bath technique is in fact a pulse-plated process in which the less noble constituent is deposited at higher overpotential or current and the more noble constituent is deposited at lower overpotential or current.

Much work[6-10] has been done based on the single bath technique. To achieve a higher practical deposition rate, Ogden[8] suggested the modulated mass transport in the plating bath in combination with current/voltage modulation. To attain sharp transition between the consecutive layers, Lashmore *et al.*[11] introduced the triple pulse technique i.e., a short zero current pulse is introduced just after high current pulse.

Besides the experimental work, a few theoretical studies have also been carried out in this field. The theoretical analysis of Roy[12] discusses electrodeposition of CMA by an electrodeposition-displacement reaction method. Theoretical equations to calculate the composition of modulated layers are al provided.

Dual Bath Technique

The dual bath technique involves t deposition in an alternate fashion, of tw constituents from separate baths. Very lit work has been done on dual ba electrodeposition. Nabirahini *et al.*[13] ha recently developed an automated compu controlled dual bath plating system f producing large-scale CMA coatings. Celis *al.*[14] have obtained Cu/Ni with distinct a continuous sub-layers by dual bath techniq

Single Bath Technique vs Dual Bath Technique

The single bath technique has the obvio advantage that the substrate always remains the electrolyte and the risk of mutual ba contamination due to substrate transfer is n possible.

Although considerable work has been do on the single bath technique, this method characterised by certain problems such displacement reactions[15,16] between the tw metallic components, which may dissol away a portion of less noble metal and repla it with more noble metal. Also, it is impossi to obtain pure deposits of less noble me layers because the noble metal alwa codeposits to some extent during the le noble metal deposition. Another limitation that the metal ions in the electrolyte shou have reduction potentials that are sufficien far apart so that nearly pure layers can selectively deposited. Thus, the selection components for CMA is limited.

The dual bath technique offers a wi choice in the selection of components a allows the deposition of components in unalloyed form. Ternary and quaternary allo can be easily electrodeposited by this metho However, the major drawback is substra transfer, which leads to bath contamination also includes different phenomena, such dissolution, reaction displacement, outsi pollution and formation of metal oxides duri the intermediate rinsing which can advers affect the properties of deposits.

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EXPERIMENTAL

For electrodeposition and characterisation of CMA, Cu-Ni system is discussed as a typical system, since Cu and Ni have the same face-centred cubic crystal structure, similar lattice parameters and well-characterised electrochemical behaviour. The bath compositions and experimental parameters are as follows: usually a sulphate electrolyte is used for the Ni bath and ethylenediamine electrolyte for the Cu bath. Other common electrolytes include zinc sulphate as crystal hydrates (80–100 g dm^{-3}) and boric acid (20–25 g dm^{-3})[17].

(i) Nickel Bath

The nickel plating bath is a standard bright Watts electrolyte – see Table I. It is prescribed because of the smooth finish obtained for nickel.

Table I Composition of Watts bath for nickel

Bright Ni	Concentration (g dm^{-3})
$NiSO_4.4H_2O$	300
H_3BO_3	40
$NiCl_2.6H_2O$	40
Coumarin	0.1
pH	4
Temperature	50±5°C

(ii) Copper Bath

For the copper electrolyte, Table II, a typical acidic copper bath based on H_2SO_4 is utilised. For good throwing power, the concentration of H_2SO_4 should be relatively high compared to the concentration of Cu.

Table II Copper electrolyte bath compostion

Bright Copper	Concentration (g dm^{-3})
Cu (as $CuSO_4$)	20
H_2SO_4	200
NaCl	0.12
pH	<1
Temperature	30±5°C

The substrates are mechanically polished and degreased in general with methanol, acetone and n-hexane. They are then activated in 1:1 HCl for 1 min. For potentiostatic deposition of Cu-Ni multilayers the optimum range for Ni is between –1.20 and –1.25 V to minimise the copper content and to prevent formation of nickel hydroxide and nickel hydride. The optimum potential range for copper is between –0.4 and –0.8 V. For galvanostatic deposition of Cu-Ni multilayers, Cu is deposited in between –1 and –3 mA cm^{-2} and nickel is deposited between –100 and –110 mA cm^{-2}.

Effect of Organic Additives

When two metals are selected, the suitable electrolyte should produce a smooth surface with a well-defined structure. Certain electrolytes particularly those containing organic additives can leave behind a thin organic layer which prevents further plating. E.g., the work of Tench *et al.*[18] shows that saccharin lowers the current efficiencies markedly at all current densities. Thus, short chain aliphatic organics such as small surfactants or inorganic acids, or solutions containing strong complexing agents (e.g. citric acid, tartaric acid, oxalic acid etc.) as typical activation systems have been suggested. Yahalom *et al.*[10] have preferred coumarin and sodium dodecyl sulphate (SDS) to minimise dendrite formation and to prevent hydrogen sheathing respectively.

Effect of Off-Time

Roy *et al.*[16] have proposed a model where the displacement reaction between Ni and Cu that occurs during the pulse off-time is related to the difference in nobility of the two metals. The more noble component, Cu is deposited at the steady state limiting current throughout the pulse cycle. Nickel, on the other hand, was plated during the pulse on-time. In other words, at longer off-times, Cu rich layers of measurable thickness can be formed on which an alloy layer of different composition is plated during the on-time. The effect of galvanic corrosion on alloy composition due to longer off-time has also been studied[15].

STRUCTURE OF ELECTRODEPOSITED CMA

Microstructural characterisation is important in order to understand the behaviour and properties of multilayered alloys. The microstructure depends on several components:

i) the nature of individual sublayers,
ii) layering and interfaces between the layers,
iii) orientation and grain size,
iv) periodicity of multilayers and
v) crystal structure.

The interfaces are described by their roughness, coherence and composition variance.

Different methods such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) for cross sectional views of arrangements of multilayers, X-ray diffraction (XRD) for crystallographic structure and the modulation wavelength, and Auger depth profiling for determination of composition of deposits are being used.

The microstructure of the multilayers observed by different techniques is described below.

SEM

Bonhote *et al.*[9] have found that the Cu-Ni multilayers plated at Cu deposition current density exhibit a waviness of the multilayers through the deposit. The results of Celis *et al.*[14] showed the distinct and continuous sublayers of Cu-Ni. They also identified the existence of an inner flat region and outer wavy or faced region. The layers in the regions are flat and parallel to the substrate respectively. Yang *et al.*[19] obtained a sharp boundary of Cu and Ni layers due to the reduction of Cu composition gradient at the interface.

TEM

Haseeb *et al.*[20] have shown that Cu/Ni multilayers grow in a columnar structure. The lateral size of the columns is in the range of 100–300 nm with few tens of micrometers of grain size. They have also observed a deformed layer on the substrate surface due to mechanical polishing treatment, which leads to formation of subgrains within an individual grain. Bonhote *et al.*[9] have demonstrated the epitaxial growth of Ni-Cu sublayers with a lateral size of 200–400 nm.

XRD

Lashmore *et al.*[11] confirmed the presence of a superlattice due to a central peak surrounded by distinct satellite peaks. The deposits obtained by Bonhote *et al.*[9] exhibit a strong <110> texture as evidenced by the large relative intensity of the peak. Celis *et al.*[21] have obtained a fibre texture of Cu-Ni CMM with (210), (111) and (110) orientations. The experimental growth of CMM has been confirmed by orientation distribution function calculations.

Yaholam *et al.*[10] determined the composition of deposits with 25 nm modulation with varying total thickness by Auger depth profiling. From the above discussions, it is clear that the multilayers with reasonably good quality of structures can be obtained by electrodeposition.

PROPERTIES OF ELECTRODEPOSITED MULTILAYERS

The properties of multilayered alloys of alternating thin nanolayers include enhanced mechanical, electrical resistivity, X-ray optical properties[22], supermodulus effect, superconductivity, improved strength, wear and corrosion resistance. The above mentioned properties are attributed to the thin film effect from the limited thickness of layers, the interface effect between the layers and the periodicity effect of multilayers[23].

Yang *et al.*[24] observed the supermodulus effect in such structures when the thickness falls below 10 nm. They have indicated an increase in supermodulus effect with decrease in thickness. Gabe[25] showed the enhancement of properties for different modulated alloy systems such as increased tensile strength and increased electrical resistivity, and Adaniya *et al.*[26] have identified the better adhesion of Zn-Fe CMA on steel.

Tensile Properties and Microhardness

Tench and White[7,18,27] investigated the tensile properties of Cu-Ni multilayers. They have indicated the twofold enhancement in tensile strength for thin layers. As the layer thicknesses in 90% Ni-10% Cu multilayered alloys decrease, the ultimate tensile strength increases. Simunovich *et al.*[28] observed an increase in knoop hardness value for thin films of Cu-Ni from 2.9 to 5.6 times the value of the individual components. The increase in the strength and microhardness of multilayered deposits was shown by Zabludovsky *et al.*[17] using the program controlled pulsed current method.

Rousseau *et al.*[29] have indicated the decrease in hardness of Cr-Ni multilayers with the increase in thickness of Cr and Ni rich sublayers and they have shown that the microhardness of Cr-Ni multilayers increases after an appropriate heat treatment (T<500°C). They also noted that the corrosion wear of multilayers is improved by the decrease of cracks. Ogden[8] and Meneze *et al.*[30] have noted the increase in tensile strength with decrease in sublayer thickness.

Corrosion Resistance

In recent years the use of zinc alloys such as Zn-Ni, Zn-Co, Zn-Fe has increased due to their superior corrosion resistance[31-34]. The corrosion behaviour was studied using corrosion potential measurements, neutral salt spray (NSS) testing as well as electrochemical and salt fog corrosion tests. XPS analyses showed that in acid and aqueous environments the corrosion resistivity of NiP/Sn interfaces[35] was due to an extremely insoluble $Sn_3(PO_4)_2$ salt. The sulphur tests revealed the superior corrosion resistance of Ag-Pd alloys[6] due to the presence of incorporated Cl in Ag-Pd CMA.

Magnetic and Electrical Resistivity Properties

The discovery of giant magneto resistance (GMR) in nanostructured multilayers containing alternating magnetic and non-magnetic multilayers opened up new horizons in the field of magnetic materials due to their enhanced magnetic properties. The GMR effect is the change in electrical resistance in response to a magnetic field. Miyazaki *et al.* have observed[36] that variation of the magneto resistance curve of Co-Cu multilayers is a function of the annealing temperature. The change from super paramagnetic to ferromagnetic properties with respect to the increase in annealing temperature has also been observed. The results of Myung *et al.*[37] show that GMR and electrical resistivity are the functions of sublayers' thicknesses. The electrical resistivity decreased monotonically as the Ni layer thickness increased while magneto resistance increased. Chassaing *et al.*[38] have observed the characteristics of a magnetic coupling between Fe-Ni layers as a result of MR; a decrease in the resistivity as a function of the applied field in both the parallel and transverse directions was observed. Celis *et al.*[35] have carried out excellent studies of the electrodeposition of magnetic layers of different systems such as hard magnetic CoPt(P) multilayers, soft magnetic Co(Sb)/Cu multilayer, Cu/Ni multilayers etc.

APPLICATIONS

Electrodeposition is an outstanding industrial technique employed in many industries. It is a versatile and an economically viable method for the synthesis of CMA. The remarkable properties exhibited by CMA find applications as listed below.

i) They can be used in optical devices such as laser mirrors or for long wavelength neutrons.
ii) Thin Cu/Ni, thin Ni/Fe CMA are important in the manufacturing of information storage devices due to their enhanced magnetic properties. They are also used for nanoscale chip circuit designs and magnetic thin films[13].
iii) Hard magnetic CoPt(P) layers are very important for technological applications in microelectro mechanical systems. [MEMS].
iv) Ag/Pb multilayers function as antifriction overcoats on magnetic hard discs.
v) Ag/Pd alloy[6] is a potential substitute for hard gold plating on electrical contacts.
vi) Ni-W CMA[39] are used in magnetic heads, bearings, magnetic relays and catalysis in the processing of oxygen–carbon-containing components.
vii) NiP/Sn multilayers are used in the petrochemical industry[35] for valves and as microelectronic components functioning in aggressive environments due to the enhanced corrosion resistance of the CMA.
viii) Besides their magnetic applications as reading-writing heads, Cu/Ni multilayers are used as temperature sensors due to their low thermal stability and low coercive field.
ix) Due to their sensitivity of electrical resistance on temperature variations Au/Co multilayers are used as temperature sensors for various technological applications.

CONCLUSION

As discussed, CMA prepared by electrodeposition have several marked advantages, which enable their use in many specific applications. The use of structures with high tensile strength is of interest to micro-mechanics. The development by Myung *et al.*[40] of the zero emission electrochemical reactor system to eliminate heavy metal waste effluents by electrodeposition is important to environmental clean-up. Advantages of this system include prevention of metal oxide formation, and complete recovery of metals, and they have obtained distinct multilayers. Thus, electrodeposition of CMA is a versatile technique with great potential for application in the microelectronics industry.

REFERENCES

1. T. Shino and T. Takada, Metallic Super Lattices, Elsevier, Amsterdam, 1987.
2. J. Chen, E.D. Rippert, S.N. Song, M.P. Ulmer and J.B. Ketterson, *J. Mater. Res.*, 1994, **9**, 1678.
3. F. Hakkens, A. Deveieman, W. Coenl and F. Den Broeder, *J. Mater. Res.*, 1993, **8**, 1019.
4. W. Blum, *Trans. Amer. Electrochem. Soc.*, 1921, **40**, 307.
5. A. Brenner, "Electrodeposition of Alloys", Academic Press, New York, 589, vol II, 1963.
6. U. Cohen, F.B. Koch and R. Sard, *J. Electrochem. Soc.*, 1983, **130**, 1987.
7. D.M. Tench and J.T. White, *Met. Trans.*, 1984, **15A**, 2039.
8. C. Ogden, *Plat. Surf. Finish.*, 1986, **5**, 130.
9. Ch. Bonhote and D. Landolt, *Electrochim. Acta*, 1997, **42**(15), 2407.
10. J. Yahalom and Ohizadok, *J. Mat. Sci.*, 1987, **22**, 499.
11. D.S. Lashmore and M.P. Dariel, *J. Electrochem. Soc.*, 1988, **135**, 1218.
12. S. Roy, *Surf. Coat. Technol.*, 1998, **105**, 202.
13. D.M.A. Nabirahni, P.T. Tang and P. Leisner, *Nano Technol.*, 1996, **7**, 134.
14. J.P. Celis, A. Haseeb and J.R. Roos, *Trans. IMF*, 1992, **70**(3), 123.
15. S. Roy, M. Matlosz and D. Landolt, *J. Electrochem. Soc.*, 1994, **141**, 1500.
16. S. Roy and D. Landolt, *J. Electrochem. Soc.*, 1995, **142**, 3021.
17. V.A. Zabludovsky, N.V. Fedotova and E.F. Shtapenko, *Trans. IMF*, 1996, **74**(3), 106.
18. D.M. Tench and J.T. White, *J. Electrochem. Soc.*, 1990, **137**, 3061.
19. C.C. Yang and H.Y. Cheh, *J. Electrochem. Soc.*, 1995, **142**, 3034.
20. A.S.M.A. Haseeb, J.P. Celis and J.R. Roos, *J. Electrochem. Soc.*, 1994, **141**, 230.
21. J.P. Celis, K. Van Acker, K. Calewaert and P. Van Houlte, *J. Electrochem. Soc.*, 1995, **142**, 70.
22. T.W. Barbee, Jr., *MRS. Bull.*, 1990, **15**, 37.
23. I.K. Schuller, *Mater. Res. Soc. Symp. Proc.*, 1988, **103**, 335.
24. W.M.C. Yang, T. Tsakalakos and J.E. Hilliard, *J. Appl. Phys.*, 1977, **48**, 876.
25. D.R. Gabe, *Electrochim. Acta*, 1994, **39**(8/9), 1121.
26. T. Adaniya, T. Hara, M. Sagivama, T. Homa and T. Watanabe, *Plat. Surf. Finish.*, 1985, **82**(3), 52.
27. D.M. Tench and J.T. White, *J. Electrochem. Soc.*, 1991, **138**, 3757.
28. D. Simunovich, M. Schlesinger and D.D. Snyder, *J. Electrochem. Soc.*, 1994, **141**, L10.
29. A. Rousseau and P. Benaben, *Plat. Surf. Finish.*, 1999, **86**(9), 106.
30. S. Meneze and D.P. Anderson, *J. Electrochem. Soc.*, 1990, **137**, 440.
31. G. Chawa, G.D. Wilcox and D.R. Gabe, *Trans. IMF*, 1998, **76**(3), 117.
32. J. Kirlova and I. Ivanov, *J. Appl. Electrochem.*, 1999, **29**, 1133.
33. G.W. Wilcox and D.R. Gabe, *Corr. Sci.*, 1993, **35**(8), 1251.
34. M.R. Kalantary, *Plat. Surf. Finish.*, 1994, **81**(6), 80.
35. J.P. Celis, P. Cavallotti, J. Machado Da Silva and A. Zielonka, *Trans. IMF*, 1998, **76**(5), 163.
36. K. Miyazaki, S. Kainuma, K. Hisatake, T. Watanabe and N. Fukumaro, *Electrochim. Acta*, 1999, **44**, 3713.
37. N.V. Myung and K. Nobe, *Plat. Surf. Finish.*, 2000, **87**(6), 125.
38. E. Chassaing, P. Nallet and M.F. Trichet, *J. Electrochem. Soc.*, 1996, **143**(5), L98.
39. N. Atanassov, K. Gencheva and M. Bratoena, *Plat. Surf. Finish.*, 1992, **84**(2), 67.
40. N.V. Myung, M. Schwartz and K. Nobe, *Plat. Surf. Finish.*, 2000, **87**(7), 76.