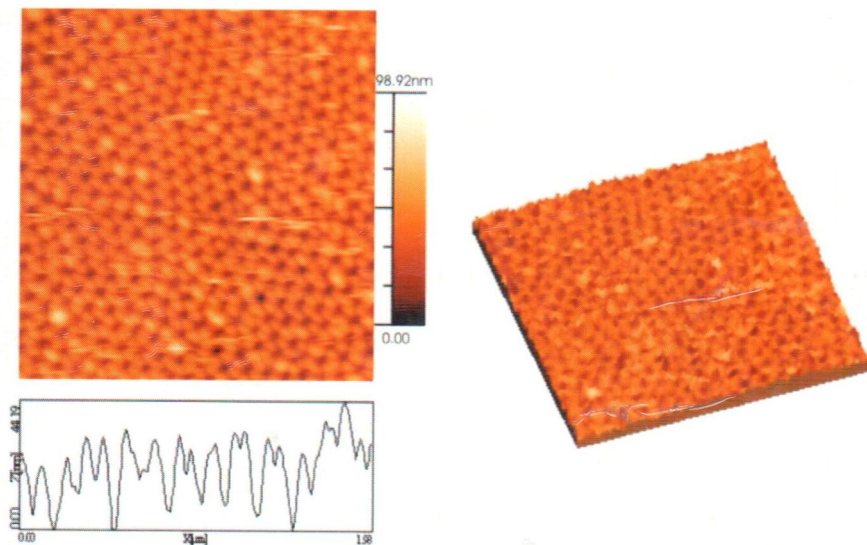# NEW DEVELOPMENTS IN ELECTRODEPOSITION AND PITTING RESEARCH
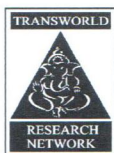
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Electrodeposition and Pitting
Research
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Electrodeposition of nanocrystalline functionally graded and multilayered deposits: Their microstructure and performance

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Abstract

The failures of engineering materials such as corrosion, friction, wear, and fatigue often take place on the surface of materials; surface properties are directly responsible for the performance of the materials. In many engineering applications, electrodeposited surface deposits are used to increase

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the lifetime of components and devices exposed to corrosion or wear conditions. Sustained environmental pressures, increasing demands for improved functional performance under more severe serving environments and emerging nanotechnology have been the driving forces for future research, innovation and process development in the field of electrodeposition and related processes. Recently, the concept of Functionally Graded Materials (FGM) and multilayered materials have been developed to achieve better anti-corrosion and longer wear life for engineering materials. This critical review presents recent status and development of electrodepositon, microstructure and practices of several new functionally graded (Ni-Co,Ni-P,Ni-W and Ni matrix composite deposits) and multilayered deposits (FGDs), which progressively make their way into the commercial marketplace and meet the ever-increasing performance demands of more severe applications.

1. Introduction

Electrodeposition as an industrial activity has been practiced for over 150 years, one of the first applications having been the electroforming of printing plates. Subsequently, electroplating gained major importance as a cheap and versatile surface finishing process for decorative applications and for corrosion and wear protection [1,2]. However, new challenges seem to emerge in parallel with the rapid development of well-established electrodeposition process. On one hand, due to ever more severe regulations concerning the emission and final disposal of heavy metal ions and chemicals, the electrodeposition industries are undergoing fundamental changes due to the environmental problems. Huge environmental pressures increasingly require that certain established plating processes be substituted by more environmental friendly technologies. The development of "clean or green" technologies in the electroplating industry is today an essential task required and initiated by environmental laws of countries around the world [3-6]. A well-known example is the replacement of cadmium, chromium and lead coatings for corrosion and wear protection by other metal or alloy coatings [3-9]. More strict environmental regulations have been coming into effect in the world. Hence, finding environmentally friendly alternatives to established electrodepositon processes is still an important general challenges.

On the other hand, as the devices, machine and structural systems serve in more extreme environments, to meet the technological demands in these areas, improved functional performance for electrodeposited deposits (e.g., anti-corrosion and anti-wear) was considerably needed. Finally, with the emergence of nanostructured materials over the last decade, electrodepositon techniques have provided a route to a variety of new nanomaterials. These include nanocrystalline deposits, nanowires, nanotubes, nanomultilayers and nanocomposites [10,11]. As the grain size of materials reduces into the

nanometer range, the materials exhibit peculiar and interesting mechanical and physical properties, e.g. increased mechanical strength, enhanced diffusivity, higher specific heat and electrical resistivity compared to conventional coarse grained counterparts [12-15].

In short, sustained environmental pressures, increasing demands form improved functional performance and emerging nanotechnology have been the driving forces for future research, innovation and process development in the field of electrodeposition and related processes. So recently, the main attentions are focused on developing new and novel deposits including the selection of green process for electrodepositon and the application of new materials in related industry. Fig.1 presents a general view of the impressive development of electrodeposited deposits over the past 150 years. It is obviously that the functional deposits evolved from the original single metal deposits, then to alloy deposits and particles-reinforced composite deposits, and finally to nanocrystalline, multilayered and gradient deposits [10,16,17]. The present review will focus on the following two subjects and related new progress:

● Functionally graded deposits with nanostructure or amorphous structure.
● Multilayered metal or alloys deposits for anti-corrosion and anti-wear applications.
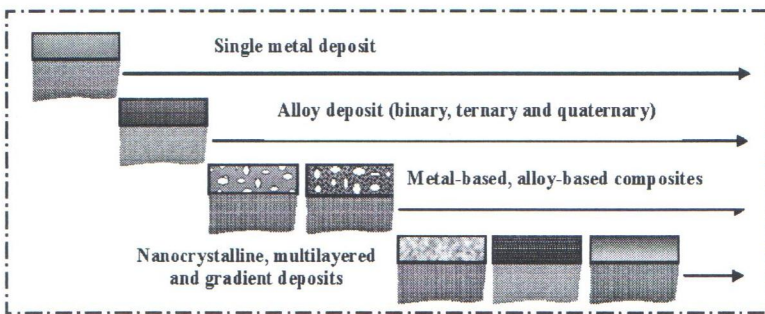

Figure 1. Development of electrodeposited deposits during the past 150 years.

2. Functionally graded Ni-Co nanocrystalline deposits with excellent tribological and electrochemical corrosion performance

Ni-Co alloys have been investigated as important engineering materials for several decades because of their unique properties, such as high strength,

good wear resistance, heat-conductive, electrocatalytic activity and specific magnetic properties [18-22]. Since friction and wear are of high concern especially in industrial components resulting in huge economic losses and sometimes catastrophic failure, and corrosion destroys more than three percent of the world's GDP (Gross domestic product) [23,24,25]. Thus, the preparation of high strength nanocrystalline with better tribological and anti-corrosion performance are needed. However, the growth of nanocrystalline alloy deposits during the electrocrystallization process was normally accompanied by the generation of high internal stress [26, 27], which directly affects the properties of deposits and may cause their cracking and peeling off from substrates. This generally restricted their applications especially for the anti-corrosion and anti-wear propose with higher thickness of deposits.

A possible approach to decrease the internal stress of electrodeposited nanocrystalline alloys is to introduce the new concept of the functionally graded materials (FGM) [28], which is aimed at achieving improvements of reliability and longevity. The idea of a FGM was substantially pushed in the early 1980s in Japan, and FGM concepts have triggered world-wide research activities and are applied to metals, ceramics and organic composites to generate improved components with superior physical properties [29-31].

Graded Ni-Co nanocrystalline alloys was produced by varying the concentration of cobalt sulfate in plating bath [28,32]. Fig.2 shows the cross-sectional SEM morphology of graded Ni-Co nanocrystalline alloy deposited on the steel substrate. It can be seen from element distribution maps that the graded Ni-Co deposits consist of six sublayers of different compositions but a smoother transition within the different layers. Composition analysis indicated that the Co content in the direction of the thickness gradually increased from 0 to 81 wt.%. The evolution of phase composition and structure of sublayer within the graded Ni-Co alloy were investigated using XRD and TEM [32]. Results showed that a continuously graded phase structure was formed with structure changed from face centered cubic (FCC) into hexagonal close packed (HCP) in the direction of thickness as a result of composition gradient within Ni-Co nanocrystalline alloys. Additionally, the average grain size in each layer was also listed in Fig.2. It is clear that the average grain size across the whole thickness was in the range of nanocrystalline range and a grain size distribution with a minimum value in the middle region and a relatively large value both in inner and outer sides.

Through above gradient design in structure and compositon, the internal stress within the as-deposited Ni-Co graded deposits decreased by a factor of about 7-10 times when compared with ungraded Co-rich deposits and it is reasonable to believe that with an accurate control of the composition and thickness of each layer within the whole deposits, the internal stress can be further reduced to a minimum level. This would be very important in the
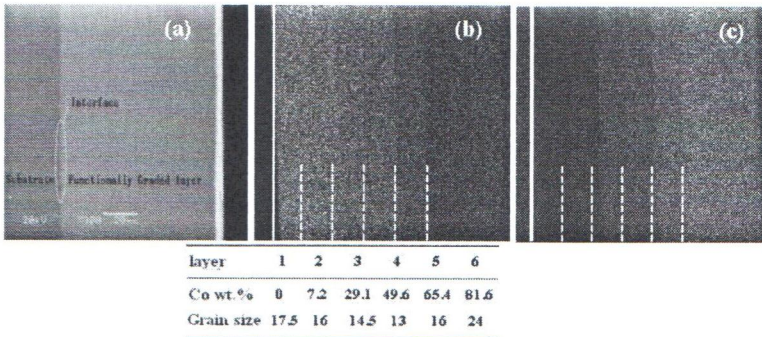
layer	1	2	3	4	5	6
Co wt.%	0	7.2	29.1	49.6	65.4	81.6
Grain size	17.5	16	14.5	13	16	24

Figure 2. (a) SEM image of the cross-section of NC Ni-Co graded deposits; (b) corresponding Ni element distribution and (c) Co element distribution map within the cross sections. Co content increased in the direction of deposit thickness. Grain size distribution exhibited a minimum value in middle region and relatively larger value in inner and outer side (reprinted from [32] with permission from Institute of Physics Publishing).

application of alloys in industry, because previous studies have shown that the fatigue life of components plated with a deposit in high tensile stress was reduced significantly, even though its adhesion was apparently unaffected.

The wear rate of as-deposited Ni-rich alloys with uniform structure and the graded nanocrystalline alloys as a function of annealing temperature in the range of 373-673K are comparatively shown in Fig.3, and corresponding variation of surface hardness with annealing temperature are shown in Fig.4. As-deposited Ni-Co gradient alloys exhibited approximately 5 times lower wear rate compared with Ni-rich alloys with uniform structure. When the annealing temperature increased to 573 K, wear rate of Ni-rich alloys increases rapidly and a large and abrupt increase in the wear rate occurred when the annealing temperature reached the 673 K. For the graded Ni-Co nanocrystalline alloys, however, it is very interesting to note that a considerably slow change (almost a plateau) of the wear rate with increasing the annealing temperature from 373 K to 673 K is displayed in spite of the fact that the surface hardness of graded Ni-Co alloys gradually decreased with annealing temperature. Obviously, graded Ni-Co alloys as annealing temperature increased up to 673 K maintained significantly improved wear resistance. Also, Ni-rich alloys with a uniform structure exhibited very high friction coefficient in the range of 0.65-0.75, while a much lower friction coefficient in the range of 0.20-0.28 was obtained for the graded Ni-Co alloys with Co-rich layer in top surface.
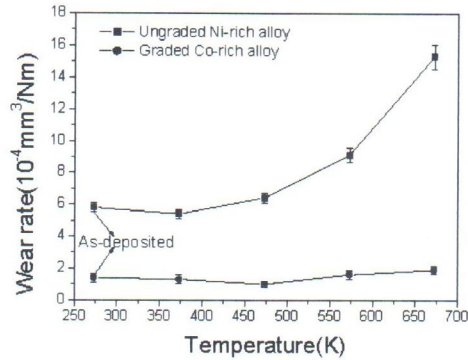
Figure 3. Wear rate of graded alloys and ungraded Ni-rich alloys as a function of annealing temperature (reprinted from [28] with permission from Institute of Physics Publishing).

Figure 4. Hardness of graded alloys and ungraded Ni-rich alloys as a function of annealing temperature (reprinted from [28] with permission from Institute of Physics Publishing).
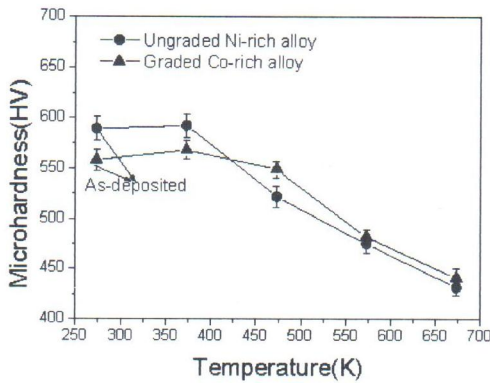
Additionally, subsequent cyclic thermal oxidation and quenching of nanocrystalline Ni-Co graded deposit results in the formation of a dense and protective CoO-rich surface oxide layer with ultrafine structure and (111) preferred orientation [32]. The electrochemical corrosion behavior of the nanocrystalline Ni-Co/CoO deposits was markedly superior compared to those of nanocrystalline Ni-Co and Ni deposits. As shown in Table 1 [32], in 10 wt.% NaOH solution, the corrosion potential positively increased from −624 to −269 mV for Ni-Co/CoO graded deposits. Moreover, the corrosion

current density of graded Ni-Co/CoO deposits is more than one order of magnitude lower than that of nanocrystalline Ni-Co deposits. Similarly, in 3.5 wt.% NaCl solution, the graded Ni-Co/ CoO deposits also exhibited much positive corrosion potential and significantly decreased corrosion current density. The significant improvement in the corrosion and tribological performance of nanocrystalline Ni-Co/CoO graded materials can be attributed to the graded microstructure within deposits, diffusional barriers to corrosion and solid lubrication effect of ultrafine CoO surface layer. Such high-performance nanocrystalline gradient alloys with superior self-lubricating performance, higher wear and corrosion resistance, will be the 'ideal' advanced materials for a wide range of functional applications.

Table 1. Corrosion potential (E_{corr}), corrosion current (i_{corr}) and polarization resistance (R_p) of nanocrystalline Ni-Co graded deposits measured in different solutions [27].

Solution	Sample	E_{corr} (mV)	i_{corr} (A cm^{-2})	R_p (kΩ cm^2)
NaOH	Ni-Co graded deposits	-624	4.53E-6	0.67
	Ni-Co/CoO graded deposits	-269	3.66E-7	6.96
NaCl	Ni-Co FGDs graded deposits	-539	3.38E-6	0.93
	Ni-Co/CoO graded deposits	-201	8.12E-7	3.53

The interesting results obtained from the design and performance of Ni-Co graded deposits provide important design principles for the fabrication of lubricating, corrosion and wear resistant nanocrystalline deposits used in the corrosion environment and tribological conditions (summarized in Fig.5). Firstly, for corrosion and tribological coatings, low internal stress and strong adhesion between coatings and substrates is critically important for long service life. Secondly, the assembly of a self-lubricating oxide layer with excellent anti-adhesion wear and anti-corrosion property are of great vital to the fabrication of such kind of high-performance nanocrystalline materials. Finally, this illustrates that corrosion resistance and tribological performance of nanocrystalline deposits can be further improved by optimizing the microstructure and composition without loss of strength and its nanostructure nature.

3. Graded Ni-P alloy deposits for replacement of conventional hard chromium

Hard chromium deposits, which have the advantage of high hardness, better corrosion resistance in extreme environments, excellent wear resistance
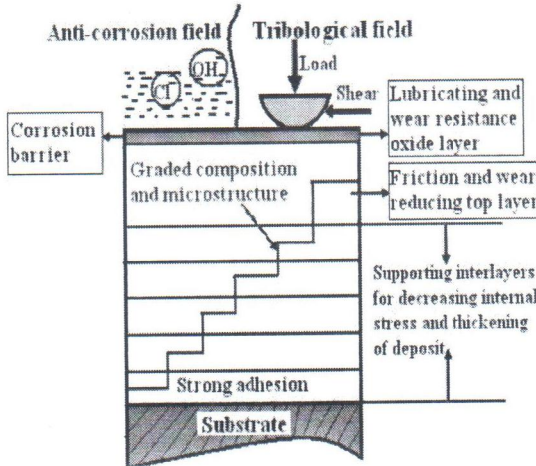
Figure 5. Fabrication and design principle for lubricating, corrosion and wear resistant nanocrystalline deposits or coatings with graded composition and structure (reprinted from [32] with permission from Institute of Physics Publishing).

and low coefficient of friction, have been widely used in the automotive, aerospace, mining and general engineering industries for application such as internal combustion engine components, hydraulic cylinders, rolls and machine tools [33-35]. However, in all environmental regulations, chromic acid (CrO_3) which is mainly used in hard Cr plating have been recognized as both highly toxic and carcinogenic chemicals, and was identified by the U.S. Environmental Protection Agency (EPA) as one of 17 "high priority" toxic chemicals. Consequently, the use of hexavalent chromates will require special waste disposal methods and expensive breathing apparatus, and exhaust systems must be employed to deal with emissions during processing [36]. Hexavalent chromium is banned from use in the manufacture of vehicles in the European Union nation's states on July 1, 2003. Moreover, European Union has passed the WEEE and ROHS directives to restrict the use of certain hazardous substances which include hexavalent chromium in electrical and electronic equipment from 1 July 2006 [4,37]. For these reasons, alternative process, substitute materials and new designs have been under study for many years.

The following Table 2 offers a summary of some of the non-chromium replacements for hard chromium process [38,57]. Many of the replacements are based on Ni and Co-based alloy or composite deposits, which has been completely reviewed by E.W. Brooman in detail [59-62]. Alternatives such as

Table 2. Summary of Non-Chromium substitutes for hard Chromium deposits.

	Possible Non-Cr Replacement	Notes	Product, Reference
Electrodeposited Ni-based alloy	Ni-W-B Ni-W	Uses conventional plating equipment and operates similar to a conventional nickel plating bath; may be more costly than hard Cr.	AMPLATE, 38,39
	Ni-W-SiC Ni-W-SiC-PTFE	May provide higher plating rates and higher cathode current efficiencies; may provide better throwing power and better wear resistance; may be more costly than hard Cr.	Takada Inc. 40,41
	Ni-Fe-Co	Vendor claims twice the wear resistance and 2.6 times the corrosion resistance of hard Cr.	Shining Surface Systems, METTEX 6 http://www.surfacesystems.com/ presentation_6.html
	Ni-W-Co Ni-W-Fe	Contains no chloride or strong chelators; can be used barrel plating good corrosion resistance except in marine environments; may tarnish; contains ammonia	Enthone, Enloy Ni-150 http://www.afonline.com/articles/ 00sum03.h tml, 42
Co-based alloy	Co-P Co-P-B$_4$C	Nano-crystalline deposit produces extreme hardness; abrasive wear resistance is better than hard Cr	Integran Technologies, Inc. http://www.integran.com/, 43
	Co-WC Ni-Co-WC	Nano-sized WC particles; similar friction coefficient wear resistance to hard Cr deposits.	44,45
	Co-W	Hardness close to hard Cr after heat-treatment	46
	Co-Cr$_3$C$_2$	Better abrasive wear resistance	47, 48
Electroless	Electroless Ni-P -Ni-W -Ni-B -Ni-P-diamond/SiC -Ni-PTFE -Ni-W-P -Ni-Co-P -Ni-Co-P-diamond	Poor abrasion resistance than hex, hardness possibly close to hard Cr after heat-treatment at high temperature. The hardness, wear and corrosion resistance depends on the composition and microstructure of alloy deposits.	49, 50, 51, 52, 53
Other methods	HVOF (high velocity oxygenated fuel) thermal sprays	Hardness and wear resistance similar hex chrome; limited to line-of-sight applications.	Sulzer Metco Western Hard Chrome 54,55,56
	Physical vapor deposition (PVD), CVD, Ion implantation, IBAD.	Greater hardness than hex chrome with a thinner coating; less corrosion resistance; deposited at high vacuum conditions and higher costs than hard process.	Southwest Research Institute, 57,58
	Laser cladding	Non-line-of-sight; nickel carbide coating	Surface Treatment Technologies

composite coatings and trivalent chromium deposits have been also investigated in recent years [4,63-65]. Unfortunately, extremely limited coatings or technologies could completely replace the conventional hard chromium coatings both in property and cost, owing to the comprehensive

properties that hard Cr deposit possesses, such as high hardness, low friction coefficient, excellent wear and corrosion resistance. As a result, many chromium alternatives can only provide good corrosion resistance rather than the comprehensive properties. For examples, a comparative study of the physicochemical and electrochemical properties of Cr and amorphous Ni-W-P electrocoatings is presented in [66]. $Ni_{65}W_{20}P_{15}$ layer exhibited a slightly superior corrosion potential then Cr deposits, and presented higher hardness when annealed at above $100^{\circ}C$. Thus $Ni_{65}W_{20}P_{15}$ is thought as a potential candidate to replace Cr in anti-corrosion applications. Similarly, Capel and his colleagues [46] have found that electrodeposited Co-W and Co-W-Fe deposits shows better corrosion resistance, but lower wear resistance and higher coefficient of friction than hard chromium.

Moreover, Narayanan and his co-workers [67] have successfully prepared the Ni-P graded coatings by sequential immersion in three different hypophosphite-reduced electroless (EL) plating baths and evaluated their corrosion resistance by polarization and electrochemical impedance spectroscopic studies. One important aspect of depositing electroless Ni–P graded coatings is the application of a nickel strike between each layer, so that the deposition proceeds without any hindrance when the substrate is sequentially immersed in electroless plating baths. The graded electroless Ni–P coatings are uniform and the compatibility between the three layers is good. The polarization curves and the Nyquist plots obtained for non-graded as well as graded electroless Ni–P coatings, in 3.5% sodium chloride solution, are shown in Fig. 6 and Fig.7, respectively.

Based on the above polarization curves and Nyquist plots, it can be observed that among the non-graded electroless Ni–P coatings, the corrosion resistance offered by electroless Ni–high P coating (EL Ni-high P) is higher than that of the other two types of coatings. Between the two types of graded Ni–P coatings, the coating that has Ni–high P (LMH) as the outer layer offers better corrosion. When electroless Ni–high P coating forms the outer layer of the graded (LMH) Ni–P coating, the corrosion resistance increases. In contrast, when electroless Ni–low P coating forms the outer layer of the graded (HML) Ni–P coating, the corrosion resistance is lower than its counterpart. However, the corrosion resistance offered by the latter type of graded coating is better than that of electroless Ni–low P coating (EL Ni-low P), due to the barrier properties of the underlying Ni–medium P and Ni–high P layers. As a result, a comparison of the corrosion resistance of all the coatings studied is of the following order:

EL **graded** *Ni-P (LMH)>EL Ni-***high** *P>El Ni-***medium** *P*
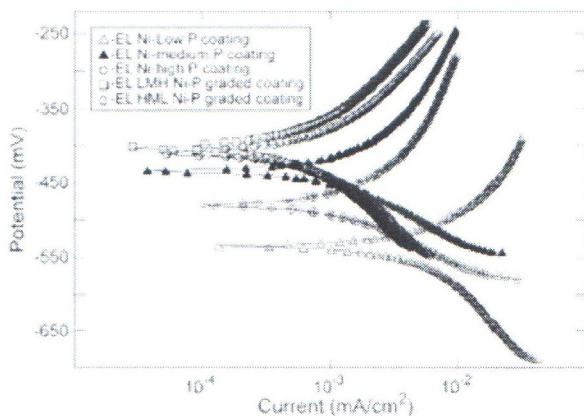*>EL* **graded** *Ni-P (HML) >EL* **Ni-low** *P*

Figure 6. Potentiodynamic polarization curves obtained for non-graded as well as graded electroless Ni–P coatings, in 3.5% sodium chloride solution (reprinted from [67] with permission from Elsevier).
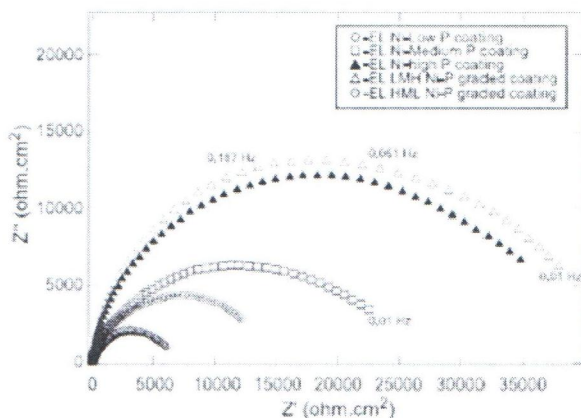

Figure 7. Nyquist plots obtained for non-graded as well as graded electroless Ni–P coatings, in 3.5% sodium chloride solution, at their respective open circuit potentials (reprinted from [67] with permission from Elsevier).

While corrosion resistance is an important properties to ensure parts, components, and products have a useful life in service, other properties also are important for these to function as designed. These additional properties include hardness and wear resistance [61,62]. However, although the hardness

of the above Ni or Co-based alloys after heat treatment are close to or even higher than that of hard Cr, however, the brittleness and the reduced integrity of alloy deposits after heat treatment restricted their applications for the replacement of hard chromium, especially for anti-wear applications with higher thickness of deposits in a progressive environment, such as under the conditions of high speed and heavy load, in which significant through-thickness cracking is observed [45,66,69].

Recently, the Ni-P gradient deposits with six layers were electrodeposited by gradually changing the current density from 5 to 30 A/dm^2 [3,69]. The distribution of P contents in as-deposited Ni-P gradient deposit and after heat treatment at 400 $^\circ$C in the direction of thickness is shown in Fig.8. It is evident that the P content decreases gradually from the coating-substrate interface to the top surface. After annealing at 400°C for 1 h, diffraction peaks corresponding to the Ni$_3$P and nickel phase were observed simultaneously, indicating the precipitation of dispersed hard Ni$_3$P intermetallic compounds in a nickel matrix. High hardness of graded Ni-P deposits in the range of 900HV-1100HV can be obtained as a result of precipitation hardening by nickel phosphide (Ni$_3$P) precipitates at high temperature [70].

Fig.9 illustrates the unlubricated wear rate of heat-treated Ni-P gradient deposit and ungraded deposits with different P contents at room temperature. It can be clearly seen that the graded Ni-P deposit shows the lowest wear rate,
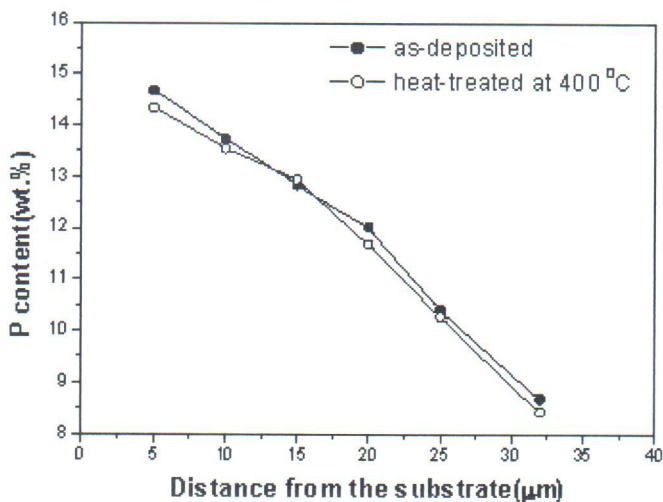

Figure 8. Distribution P content in graded Ni-P deposit both in as-deposited and heat-treated conditions (reprinted from [3] with permission from Elsevier).
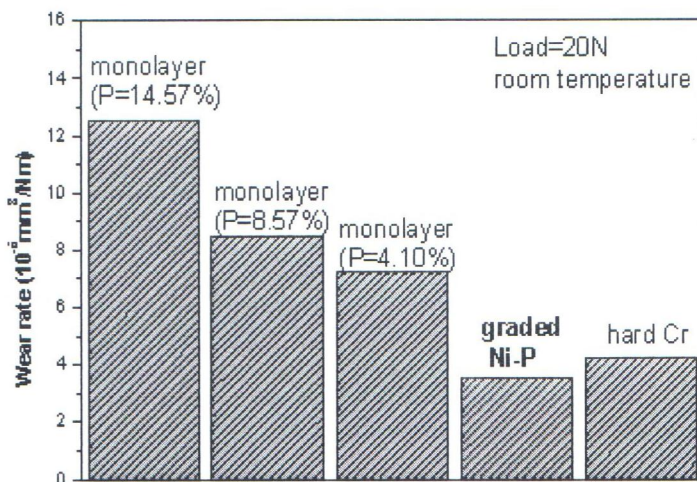
Figure 9. Wear rate of heat-treated Ni-P deposits at room temperature under dry wear conditions (reprinted from [69] with permission from Elsevier).

1/3-1/2 that of ungraded Ni-P deposits, and 15% lower than that of a conventional hard Cr deposit. It is interesting to point out that the graded changes in composition and microstructure could improve the wear resistance of heat-treated Ni-P deposits. Most important is that under dry sliding wear conditions, the graded Ni-P deposit exhibited better wear resistance compared to the conventional hard Cr deposits.

SEM micrographs demonstrated that brittle detachment and cracks were observed on the wear track of both ungraded and graded Ni-P deposits [69]. Near the sides of the wear track, extension of the cracks during the wear process leads to the formation of a network of linear cracks. These linear cracks within the wear scar or alongside the wear track may be attributed to the brittle and hardened Ni_3P precipitation as mentioned above. However, a significant improvement in wear resistance of graded Ni-P deposits was observed from SEM images of the worn surface. The crack density on the wear track of the ungraded deposits was larger than that of graded Ni-P deposits. Moreover, brittle cracks which are both parallel and normal to the sliding direction are very deep and wide, while shallow and narrow cracks were observed alongside the wear track of graded Ni-P deposits. In addition, the wear scar of the ungraded deposits is characterized by a more intense brittle detachment of debris from the deposits in the form of flakes, which results in larger wear rate. However, only some small chipping failure occurred on the

graded Ni-P deposits. Furthermore, the large deposit thickness, in combination with their brittleness and the damage effect exerted by the combined stresses of compression and shear during the wear process at room temperature results in the formation of large through-thickness cracks within the ungraded deposits (as shown in Fig.10). Once such through-thickness cracks have been produced, subsequent crack propagation under the cyclic fatigue process will eventually lead to the larger wear debris particles [71,72], and hence further wear loss is quite rapid and often catastrophic. For the graded Ni-P deposits, through-thickness cracks were effectively inhibited due to the introduction of the gradient composition within the deposit [69]; relatively fine cracks were formed both on and alongside the wear track of the graded deposit, thus preventing catastrophic failure under the heavy load. As a consequence, the heat-treated Ni-P gradient deposits exhibited better wear resistance than ungraded deposit with a uniform composition and structure.

Furthermore, high temperature friction and wear properties of the graded Ni-P deposits were tested in comparison to conventional hard Cr deposits. Fig.11 comparatively shows the hardness of graded Ni-P alloys and electrodeposited Cr deposits after heating to different temperatures. The hardness of the conventional hard Cr decreased progressively with an increase in heat treatment temperature. On the other hand, the hardness of graded Ni-P alloys increased with temperature to approximately 400 °C and then decreased moderately at higher temperatures, but was still higher than that of Cr deposits.
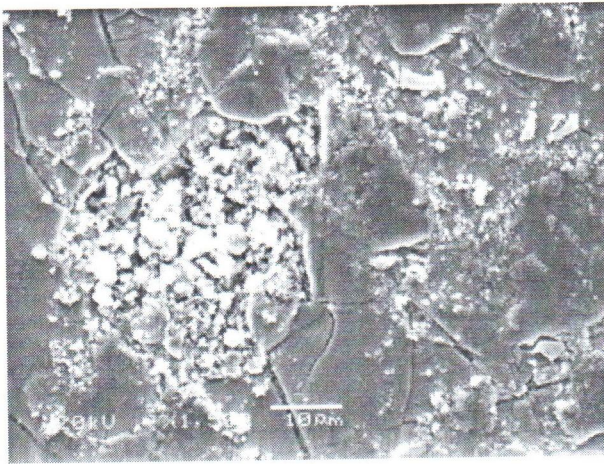

Figure 10. SEM micrograph of the worn surface of ungraded Ni-P deposits, indicating the formation of large through-thickness cracks (reprinted from [69] with permission from Elsevier).
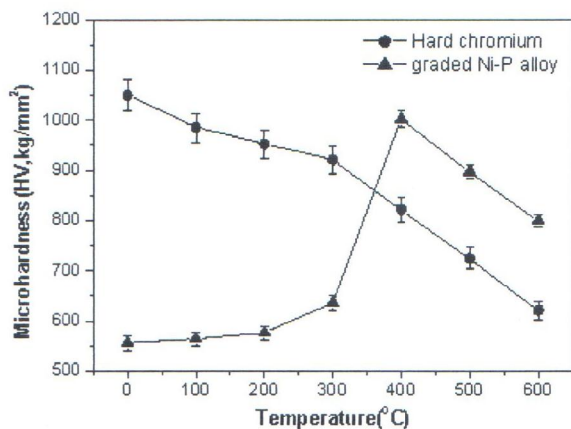
Figure 11. Variation of hardness with annealing temperature for graded Ni-P deposits (▲) and hard Cr deposit (●) (reprinted from [69] with permission from Elsevier).
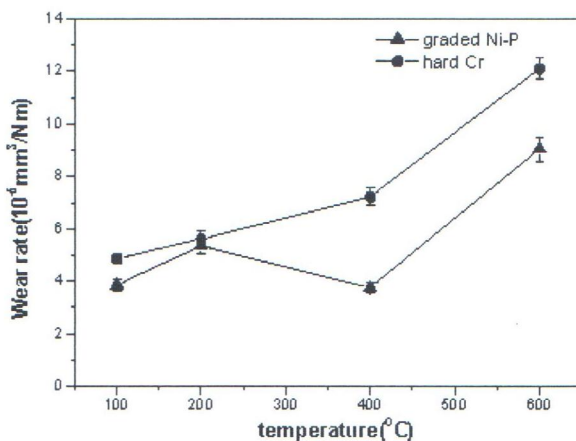

Figure 12. Effect of temperature on wear rate of heat-treated Ni-P gradient deposits (▲) and hard Cr deposit (●) (reprinted from [69] with permission from Elsevier).

Fig.12 shows the effects of temperature on the wear rates of the heat-treated Ni-P gradient alloys and conventional hard Cr deposits. The wear rate of hard Cr deposits increased with the increase in temperature. The wear rate of graded deposits at 400 °C was approximately half of that of the conventionally hard Cr deposits. With further increasing of the temperature up to 600 °C, wear rates

of both deposits increased significantly, most likely caused by the softening as a result of a test temperature higher than 400 °C. However, the wear rate of graded Ni-P deposits were much lower than that of hard Cr deposit even in the range of 400-600 °C. Consequently, graded Ni-P deposits show better wear resistance both at room temperature and high temperature conditions than conventional hard Cr deposits.

Further investigation on the corrosion resistance of Ni-P graded deposits indicated that heat treatment of graded Ni-P deposits in air show positive effect on the anticorrosion properties of deposits due to the formation of Ni_3P and Ni oxide and the heat-treated Ni-P gradient deposits with the maximum hardness also exhibited more than two orders of magnitude higher corrosion resistance against the Cl⁻ attack in acids [3]. In some applications, due to high strain rates and pressures (normally 100 MPa to 3GPa) the damage owing to cavitation erosion is very serious. Appropriate surface protective with high pressure dynamic load resistance was expected. Fauser et al. [73] prepared the Ni-P gradient deposits by electrodeposition and used the simulation tool to determine the optimal gradient layers for improved load resistance. Results show that high pressure load resistance of Ni-P can be improved by the optimised gradient design. Thus, graded Ni-P deposits may be a potential alternative to hard Cr deposits in terms of both corrosion resistance and wear resistance under less progressive environment.

4. Graded electrodeposits for other applications

The interest in electrodeposition of Ni–W alloys has increased in recent years due to their unique combination of tribological, magnetic, electrical and electro-erosion properties. These alloys exhibit good mechanical properties (e.g., high tensile strength and premium hardness, as well as superior abrasion resistance), good resistance to strong oxidizing acids, and high thermal stability to be used as protective coatings for glass molding die, oil pressurized parts and valves [74-76]. However, high thermal stress and failure due to high temperature is a major problem for the application of Ni-W deposits at high temperatures.

Yao and Wang have done lots of interesting research work on the preparation of gradient Ni-W alloy deposit. The Ni–W gradient deposit with nanostructure is prepared from plating bath contained sodiumtungsten, nickel sulfate and citrate by controlling the bath temperature and current density [77,78]. The W content in the gradient deposit increases from 12.8 to 55.1% with increasing of thickness of the deposit. X-ray diffraction indicate that crystallite size of the deposit decreases from 10.89 to 1.54 nm and lattice strain increases with the increase of W content in the direction of deposition. The profile of the Ni–W gradient deposit across the thickness was analyzed by XRD (Fig.13). It is note that the structure of the deposit changes from nanostructure to amorphous stepwise with increase in thickness of deposits.
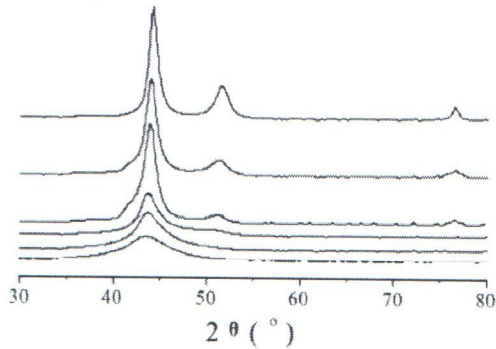
Figure 13. Microstructure change of Ni–W gradient deposit in the direction of thickness (reprinted from [77] with permission from Elsevier).

Furthermore, thermal strain distribution in the Ni–W gradient deposit is also studied by the digital-image correlation method (DICM) [77]. Fig. 14 shows the thermal strain distribution of the Ni–W deposit. The thermal strain has not obviously changed from the deposit surface (x=0µm) to the coating-substrate interface (x=298µm), then it increases sharply at the interface. Sharp increasing of the thermal strain resulting from mismatch of expansion coefficients at the interface leads to the breakage of the deposits at high temperature. Fig. 15 shows the thermal strain distribution curve of the Ni–W gradient deposit. It is concluded that the thermal strain increases gradually from the deposit surface (x=0µm) to the substrate Cu (x=330µm) and then decreases slightly in the substrate. Experimental results show that the Ni–W gradient deposit could eliminate the mismatch of expansion coefficients at the interface, and therefore relax the thermal stress of the deposits [77]. As a result, the Ni-W gradient deposits exhibited better high-temperature oxidation resistance, suitable for the high temperature oxidation circumstances [78].

Zn-based alloy deposits including Zn-Ni and Zn-Fe have been widely used to provide better corrosion protection than that provided by pure zinc deposits [79-81]. In anti-corrosion applications, they are actually regarded as having the great potential to replace electrodeposited cadmium, the use of which has been strictly regulated [80]. The duplex Zn alloy deposits with high and low zinc content layers have also been found to provide improved weldability and paintability. The sudden change in the composition at the interface between the two alloy deposits, however, led to the weak adhesion. A gradient alloy deposit may provide a solution to this problem. Four gradient Zn alloys (Zn-Ni, Zn-Fe, Zn-Ni-P, and Zn-Fe-P) were produced by continuously varying the rotation speed and applied voltage using a rotating disc electrode [82]. The results
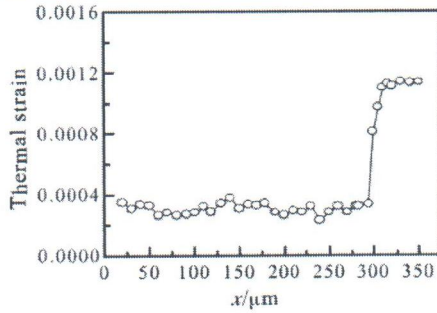
Figure 14. The thermal strain distribution of the Ni–W deposit (reprinted from [77] with permission from Elsevier).
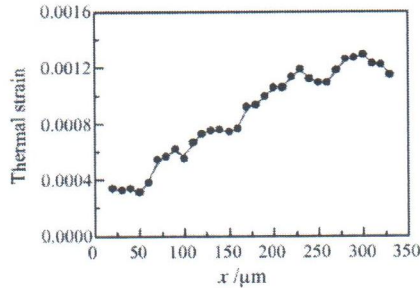

Figure 15. The thermal strain distribution of the Ni–W gradient deposit (reprinted from [77] with permission from Elsevier).

indicated that the corrosion resistance and deposit adhesion strength for all four gradient Zn alloys deposits were superior to those of conventional duplex Zn alloys.

Electrodeposited composite coatings have been widely developed over the past decades for various engineering applications due to their enhanced hardness, wear and corrosion resistance when compared to pure metal or alloy. With combining the properties of heterogeneous matrix metal and various kinds of particles, many new function materials were produced with more comprehensive applications [65]. By using composite electroplating, careful modulation of the deposition conditions can lead to metal deposits with a non-uniform, gradient or a layered distribution of incorporated particles. Examples include the discretely stepped Ni-Al$_2$O$_3$ elecrocomposite [83], bilayer Ni-SiC composite coatings [84], Ni-SiC gradient deposit [85], and Ni-ZrO$_2$ gradient coatings [86]. The gradient distribution of particles in the metal deposit can be

achieved in a single electrolyte bath by simple alterations of the current density or potential and/or by changing of stirring rate and concentration of particles in the bath. For example, by varying the degree of compressed air agitation in the bath, multilayers of nickel containing different quantities and sizes of SiC particles were achieved [87,88]. The resulting nickel deposit was shown to contain three different layers: (1) under static bath conditions, 0.7–1.1 vol.% of SiC; (2) under intermediate hydrodynamic conditions, 9.2–11.8 vol.% finely dispersed SiC; and (3) under intensive hydrodynamic conditions, 12.6 vol.% coarse SiC. A more recent investigation controlled the influence of particle concentration ($0-150$ g dm^{-3}), current density ($1-5A$ dm^{-2}) and electrode rotation (600–1200 rpm) to produce a continuous gradient distribution of SiC (7–9 µm) in a nickel deposit [85]. The obtained Ni-SiC gradient deposit with continuous distribution of the SiC content from 0 to 30 vol.% exhibited good malleability and better wear resistance performance.

The Ni-ZrO$_2$ gradient deposit with continuous distribution of ZrO$_2$ (about 1 µm particle size) content from 0 to 21% in the direction of thickness was prepared at a constant current density with increasing the particles loading content in the bath from 0 to 200 g/L [89]. The toughness of graded Ni-ZrO$_2$ deposit was studied by the impingement test. In the adjacent to the substrate, the material has good plastic deformation, which exhibits a high degree of toughness. With the increase of the deposit thickness, the toughness of the middle zone of the fracture decreases. The outer fracture adjacent to the deposit surface shows that the toughness of the deposit surface is lowest at the surface. Thus, the toughness of graded Ni-ZrO$_2$ deposits increase gradually from the surface to the matrix, and its malleability is 2.5 times as much as that of the Ni-ZrO$_2$ composite deposits because of the gradient distribution of toughness.

Single and mixed particles (1–4 µm Al conductive particles and 0.6 µm–0.8 µm α-Al$_2$O$_3$ non-conductive nanoparticles) in a nickel deposit were produced by varying the current density and concentration of particles in the plating bath [83]. A gradient distribution of Al from 12 to 9 vol.% and α-Al$_2$O$_3$ particles from 0 to 24 vol.% in a nickel deposit, achieved by constant current deposition with varied concentration of particles in the bath. The Knoop hardness of the Ni-Al-Al$_2$O$_3$ gradient composite deposits increases gradually from approximately 300 to 700 in the direction of growth of the deposit [90].

Some new technique for fabricating graded composite coatings was also presented recently. According to the electrodeposition principle, the deposition conditions can be changed when the relative position between anode and cathode is altered. Dong et al. used a regular octagonal cathode for electrodeposion of graded Ni-Al$_2$O$_3$ graded coatings by changing the relative position between anode and cathode [91]. Through the rotation of the cathode regularly, a graded composites coating with varying volume percent of aluminium oxide along the thickness is fabricated (Fig.16). The major advantages of this method are the
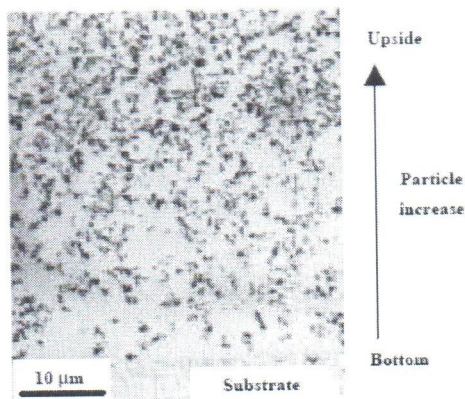
Figure 16. Cross-sectional microstructure of graded composite coating (reprinted from [91] with permission from Elsevier).

simplicity to control and the low equipment cost at low temperature. The results obtained should have significant potential for the economic mass production of a wide variety of composite coatings.

The undesired deposition of microorganisms and the formation of biofilms are called 'biofouling' [92]. Biofouling has been recognized as a widespread problem in design and operation of processing equipment such as heat exchangers, cooling water systems and food processing equipment, which will reduce the performance of processing equipment and reduce product safety through bio-contamination [93]. Ni-P-PTFE composite coatings were normally used to reduce fouling and biofouling [94]. However, the adhesion of standard Ni-P-PTFE coatings to the substrate needs to be improved, since the coatings were generally found to peel-off during fouling tests. Zhao and Müller-Steinhagen et al. [93,94] have recently developed a gradient composite coating method by gradually increasing the PTFE content from the substrate to top surface, the coating adhesion is improved significantly. This kind of graded Ni-P-PTFE coating exhibited excellent anti-bacterial behavior. Biofouling experiments show that the attachment of thermophilic streptococci on graded could be reduced by 82-97%. The photo of cells attached on the original and graded Ni-P-PTFE coated surface is shown in Fig.17. Furthermore, It has been found that these graded electroless Ni-P-PTFE coatings can reduce the formation of $CaSO_4$ deposits on heat exchanger surfaces significantly [94]. Thus, graded electroless Ni-P-PTFE coatings have a tremendous potential for reducing water scaling or biofouling formation on heat exchangers and food processing equipments.
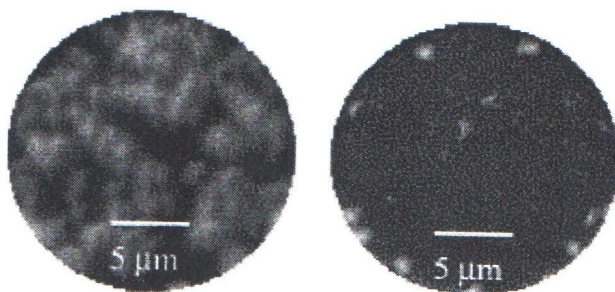
Figure 17. Biofouling experiments results; (a) a large amount of bacteria attached on untreated surface (5.6×10^5 cells/cm^{-2}). (b) few bacteria attached on graded electroless Ni-P-PTFE coated surface (3×10^3 cells/cm^{-2}) (reprinted from [93] with permission from Elsevier).

5. Multilayed alloy coatings produced by electrodeposition

A new type of coating systems so-called compositionally modulated multilayers (CMM) has been gradually gaining interest amongst researchers, because these layered-structure coatings possess improved properties or novel phenomenon such as increased mechanical strength, microhardness, giant magnetoresistance and corrosion resistance [95–100]. CMM coatings consist of a large number of thin laminar deposits of metal or alloy layers and each layer has its own distinctive role in achieving preferred performances. There are mainly two techniques used for electrodeposition of multilayers involing: (□) dual bath; and (□) single bath. These techniques have been exploited by many researchers for electro-deposition of various multilayers such as Cu/Ni [95], Ni/Sn [96], Co/Pt [97], Co/Cu [98], Cu/Ag [99], and Cu/Ni-P [100]. Among these, the tribological performance of these metallic multilayered coatings has attracted the interest of many scientists. Several papers [95,101,102] have found that multilayered Cu/Ni coatings produced by electrodeposition showed better wear resistance than homogeneous coatings of Ni and Cu and the tribological behavior was found to be dependent on the wavelength of CMM coatings. Afterwards, attempts on the electrodepositon of compositionally modulated alloy multiplayer (CMAM) coatings were made by depositing alloy sublayers under different plating conditions from single bath. Svensson' work [103] have indicated that compositionally modulated Co–W nanocrystalline alloys (three different wavelengths: 2nm, 20nm and 200nm, respectively) can be obtained from a single ammoniacal electrolyte by current modulation and the use of anodic pulses during deposition, i.e. selective

etching. The multilayered Ni-P-W coatings consisted of layers with high and low W content had been deposited by pulse plating [104-106], detailed investigation have been carried out on the microstructrue, hardness, and both the dry and lubricated sliding wear behavior of such Ni-P-W multilayers with different wavelengths (Fig.18). They observed that coatings with a smaller layer periodicity showed a better wear resistance than those with larger layer periodicities. The increased wear resistance of the small layer periodicity coatings (up to 60 nm) is attributed to the increased number of interfaces in their structure compared to the larger layer periodicity coatings, which make the cracks deflect, absorbing more energy during their the toughness of the coating [107].

During last decades, electrodeposition of CMM coatings for protection of steel substrate from corrosion has been extensively investigated. Chawa et al. [108] reported that the corrosion resistance of zinc–nickel CMM coatings obtained electrodeposited from zinc sulphate and nickel sulfamate baths was better than that of zinc or nickel monolithic coatings of a similar thickness. Ivanov et al. [109] studied the corrosion performance of zinc–nickel CMM coatings with the total thickness of 12 μm obtained by successive deposition from dual baths mainly using anode potentiodynamic dissolution method. To date, however, relatively few reports have given any evidences to "back-up" the enhanced corrosion resistance afforded by Zn–Ni CMM coatings. Fei and Wilcox [110] have prepared the Zn–Ni CMM coatings by successive deposition from dual baths containing a Zn sulphate electrolyte and a Ni–ammonia complexed electrolyte. Fig. 19 illustrates a typical cross-sectional morphology of a 12-layer Zn–Ni CMM coating with Zn sublayer adjacent to
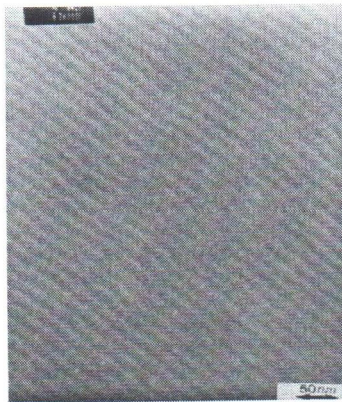

Figure 18. Cross-sectional TEM micrograph of a multilayered Ni-P-W coating (wavelength =6nm). The low-W layers are the light layers and the high-W layers are the dark ones (reprinted from [106] with permission from Elsevier).
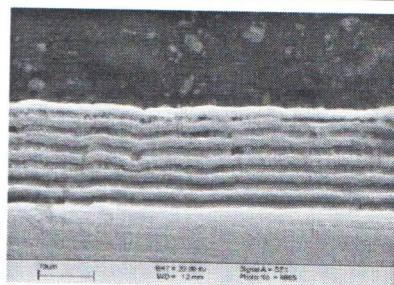
Figure 19. Cross-sectional morphology of Zn/Ni CMM coating with 12 individual layers (reprinted from [110] with permission from Elsevier).

the substrate and Ni as the top layer. Corrosion resistance evaluated by means of neutral salt spray test showed that Zn-Ni CMM coatings were more corrosion-resistant than the monolithic coating of Zn or Ni of similar thickness and the Zn-Ni CMM coatings with a nickel sublayer adjacent to the steel substrate and zinc as the top layer have the best protective performance. Based on results from electrochemical measurement and the micrographic characteristics of Zn-Ni CMM coatings after corrosion testing, a probable corrosion mechanism of Zn-Ni CMM coatings was proposed in Fig.20. Diagrams A and B show the structures of two Ni/Zn CMM coatings with different individual layer thicknesses. Initially, Zn top layers corrode completely, and then the Zn sublayers dissolve through the pores in the Ni sublayers. Diagrams C and D exhibit the structures of two Zn/Ni CMM coatings with different individual layer thicknesses. The Zn sublayer beneath the Ni top layer dissolves through the pores existed in the Ni deposits during corrosion process. As a whole, the protection efficacy of Zn-Ni CMM coatings may be thought to depend on the barrier effect of the Ni sublayers and the sacrificial effect of Zn sublayers.

Cadmium deposits have been used for years as a corrosion resistant coating in electrical, aerospace and fastener industries owing to its excellent corrosion resistance and engineering properties [111]. Efforts have been made to find a suitable alternative because of toxicity of metal and its salts, risk of failure due to hydrogen embitterment and to avoid cyanide baths for cadmium plating [112]. Recently, compositionally modulated Zn–Ni alloy deposits were also deposited from acidic bath on carbon steel substrates and the nickel content was varied as a function of thickness by applying a varying potential sequence [113]. The electrochemical and corrosion tests suggested that the CMM Zn–Ni multilayer with 20 wt.% Ni can be considered as an alternate to the conventional Zn–Ni with 8–15 wt.% Ni and commercial cadmium coatings.
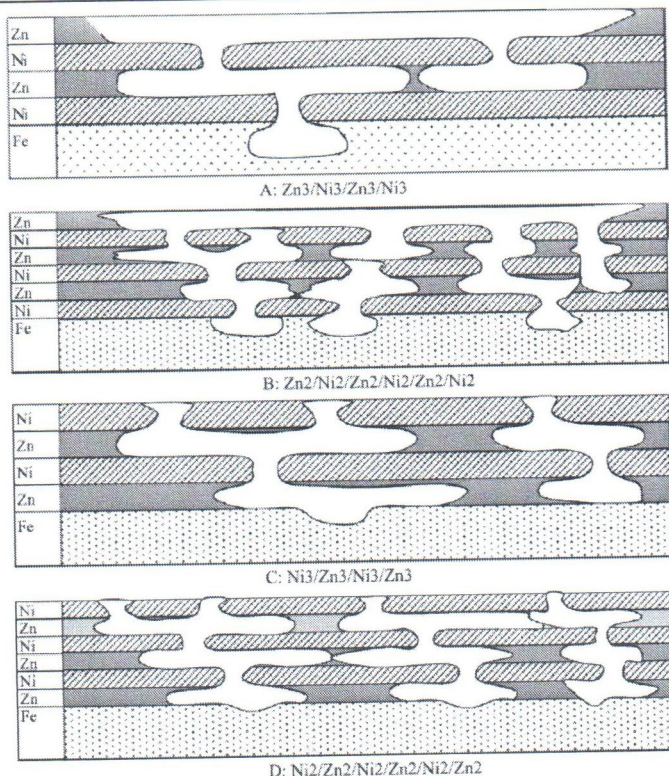
Figure 20. Corrosion mechanism diagram for Ni/Zn and Zn/Ni CMM coatings (reprinted from [110] with permission from Elsevier).

Electroless deposition Ni–P alloy coating does have widely commercial applications in many fields because of its excellent properties. However, since the corrosion potential of Ni–P coating on steel is more positive than that of steel substrate, the Ni–P alloy coating on steel substrate is the non-sacrificial coating. Based on the fact that the corrosion potential of Ni–P alloy varies remarkably with the phosphorus content, several multilayer coatings (two layers and three layers) prepared by combining electrodeposition with electroless deposition [114], were designed to realize an effective electrochemical or sacrificial protective coating on steel substrate. The salt spray tests and polarization curve analysis indicated that, among these coatings, the coating of three layers with a thin electroplated Ni layer sandwiched into the two-layer Ni–P alloy coatings [from surface to substrate: Ni–P (low phosphorus)/Ni/Ni–P

(high phosphorus)] performed excellent corrosion resistance. In the salt spray test, the time of the emergence of the first red rust spot of the multilayer coating is about 936 h, which is 3.5 times of that of Ni–P alloy coating with high phosphorus content. Therefore, the designed three-layer coating provided an effective electrochemical protection for the steel substrate. Studies on the electroless Ni-P/Ni-B multilayered coatings demonstrated that the obtained multilayers exhibited better wear and corrosion resistance than Ni-P and Ni-B coatings of similar thickness [115], which claimed that if higher hardness and wear resistance are desired, then the multilayer coating having Ni-B as the outer layer will be the ideal choice whereas the multilayer coatings having Ni-P as the outer layer is the preferred option where higher corrosion resistance is sought.

Nd-Fe-B permanent magnet was developed in the 1980s with excellent magnetic properties such as high remanence, high coercivity, and large maximum energy product. The major drawback that has prevented its wide spread application is its low corrosion resistance in humid and chloride environment. To overcome this problem, a lot of research work on the protective coating on Nd-Fe-B magnet has been carried out [116,117]. Recently, Chen et al. [118] explores the possibility of using electroless Ni-P plating for the protection of powder sintered Nd-Fe-B permanent magnet, because there has been little investigation on electroless Ni-P application on Nd–Fe–B magnet. The reason for this is that medium-and high phosphorus content of electroless Ni-P for corrosion protection is usually achieved in acidic solutions of pH around 4.8 [119]. However Nd-Fe-B reacts quickly with Cl^- and SO_4^{2-} in acidic solutions. The approach adopted in their study is to deposit an intermediate layer of Ni-P in an alkaline solution first. This intermediate layer itself is not enough to provide the needed corrosion protection, since it is not dense enough and only contains a low percentage of phosphorus. The role of this layer is to provide a platable surface for the corrosion-resistant Ni-P coatings plated in the conventional acidic solutions. Finally, protection of power-sintered Nd-Fe-B magnet was successfully achieved by an intermediate coating in alkaline solution followed by high-or high-/medium-phosphorus coatings in acidic solutions. The phosphorus content for low-, medium- and high-phosphorus coatings are 2.5–3.0, 6.7, and 11.1 wt.%, respectively. Corrosion experiment shows that excellent corrosion resistance was obtained for above multilayered Ni-P coatings. Although there is a loss in magnetic properties after the Ni-P multilayer, but remaining values are still very attractive for practical applications [116].

6. Summary and conclusions

The new concept of functionally graded deposits (FGDs) and multilayered materials have been developed to achieve better anti-corrosion and longer wear

life for engineering materials. The electrodeposition techniques compared with other methods have enabled the fabrication of such kind of functionally protective deposits, which possess a wide range of comprehensive properties and optimum performance not available with pure metal or alloy deposits. The gradient and multilayer design in composition and microstructure can give: (i) a decreased internal stress during electrodeposition process or thermal stress during the heat-treatment and thus better adhesion strength with substrates (for corrosion and tribological coatings, low internal stress and strong adhesion between coatings and substrates is critically important for long service life.) (ii) an increased strength, toughness and improved impact load resistance, thus the increased corrosion, wear and high temperature oxidation resistance which can be further enhanced with nanostructure. These newly-emerged nanocrystalline graded or multilayered deposits will meet the ever-increasing performance demands of more severe applications. Results presented in this review provided important design examples for the fabrication of special-structured deposits used in the corrosion environment and tribological conditions. In which, control of the structure and composition of deposit is an exciting scientific subject combined with an industrial challenge. In a sense this demonstrates that the micro-controlled electrodeposition process can allow researchers and engineers to specify the surface properties which they needed and to make full use of novel concepts used in design system for advanced materials. In addition, the fabrication of functionally graded deposits by electrodeposition methods has the advantages of versatility, ability to coat complex shapes and low cost.

Acknowledgement

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