JCSE The Journal of Corrosion Science and Engineering
21st Century Corrosion Science
Volume 6 Paper C126

Surface Modification With Compositionally Modulated Multilayer Coatings

G.D.Wilcox
Institute of Polymer Technology and Materials Engineering,
Loughborough University,
Loughborough,
Leicestershire. LE11 3TU.
UK, G.D.Wilcox@lboro.ac.uk

Abstract
The concept of compositionally modulated multilayer coatings (CMMCs) is one that is gaining considerable interest in surface engineering, whether the end use is for wear resistance or protection against corrosive environments. Multilayer finishes are by no means a new coating format since layered coatings have traditionally been used in surface engineering e.g. decorative chromium and traditional paint finishes. Where the more recent CMMC concept differs is usually in the number of individual layers and hence their relatively small thicknesses.

The CMMC concept can be produced quite readily by electrodeposition, either with a dual bath or single bath approach. The dual bath approach is physically more complex with the substrate moving between two electrolytes, with appropriate rinsing in between. The single bath concept is more complex in terms of solution chemistry and control of electrodeposition process parameters to produce the layered deposit required.

This paper will examine the concept of the production of CMMCs, concentrating on their application as protective coatings for metal surfaces. The application of zinc and zinc alloy based systems will be investigated as this is one particular area of interest for this type of coating system. Of the zinc alloys that can be electrodeposited, at present, Zn-Ni, Zn-Fe, Zn-Co and Zn-Mn have been produced in multilayer format. The results from these investigations will be reviewed. Electrodeposition methods, bath chemistries and coating morphologies and performances in appropriate corrosion tests will also be reviewed.

Keywords: Compositionally modulated coatings, layered coatings, zinc alloys

Introduction
The concept of compositionally modulated multilayer coatings (CMMCs) is one that is producing a high level of interest in surface engineering. The subject area is one that abounds with terminology, with the coating systems produced often being described as compositionally modulated alloy (CMA) coatings, multilayer coatings or just layered coatings. Whatever the terminology used to describe them, the overall structure can be regarded as a coating system with individual layers (usually two compositions repeated) making up the overall structure. Figure 1 illustrates a typical CMMC system.

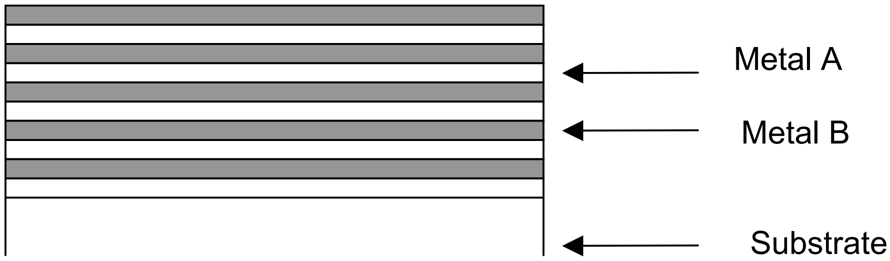


Figure 1 Idealised schematic of a compositionally modulated multilayer coating

Metal A and metal B in figure 1 are different in composition. They can be individual 'pure' metals or two different compositions of the same alloy. The CMMC therefore has a periodicity associated with its coating structure, the periodic distance being the thickness of the two coating formats (i.e. one metal A layer + one metal B layer in figure 1). Individual layer thicknesses for CMMC systems range from a few nanometres to tens of microns, these values being dependent on the coating system type and its end use.

The concept of multilayer coatings is not new, if one examines the historical use of surface treatments it becomes apparent that sometimes by design and sometimes by accident, many familiar coating systems are multilayer in their format. Some of the earliest examples can be seen in the use of 'underlayers' or 'undercoats'. Copper has been used historically under nickel layers primarily for adhesion purposes. In a similar manner nickel itself has been used with silver and gold layers. Electrodeposited decorative chromium is another example of a multilayer system with an initial 'flash' layer of copper, duplex nickel layers for corrosion resistance and an upper thin layer of chromium for decorative purposes. Similar situations can be seen with organic finishes such as paints and lacquers (figure 2). Most of these utilise a conversion coating pre-treatment before being applied to a metallic substrate. The organic systems themselves are then usually multilayered with a primer layer, undercoat and top coat. Another example of a multilayered format in surface treatments occurs indirectly but can be utilised to good effect, this is the occurrence of different compositioned alloy layers occurring at the coating-substrate interface in hot dipped or heat-treated metallic coatings. These occur as a result of the enhanced temperature levels present during the formation of the coating and often lead to enhanced corrosion resistance (e.g. in flow-melted tinplate used in the food packaging industry [1]).

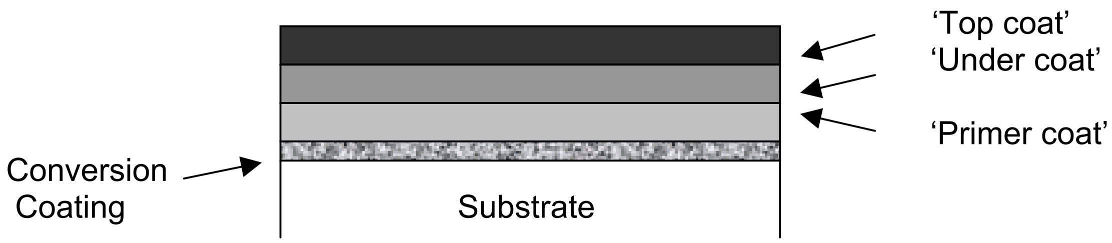


Figure 2 Multilayer concept in organic paint coatings

The modern versions of CMMCs tend to have a greater number of individual layers, consequently of smaller individual layer thicknesses. The more recent interest in CMMCs is often attributed to Koehler, a theoretical physicist interested in dislocation theory, who showed, in principle, that an array of thin films could produce enhanced mechanical properties such as tensile strength, Young's Modulus and hardness [2]. He predicted that for this situation to occur, the following criteria must be met for the two individual metals making up the layered structure:

- Similar lattice parameters
- Similar thermal expansions
- Very dissimilar elastic constants
- The bonding between dissimilar metal atoms should be large and the same order as that between themselves
- The thicknesses of the layers should be small, typically less than 100 atoms thick.

Koehler also suggested some near 'ideal' metal pairings: Ni-Cu, Rh-Pd, Pt-Ir and W-Ta. The individual layer thicknesses are often on the nanometre scale, this therefore limits the deposition technologies for this type of coating. In reality there are probably only three main methods which have been utilised namely, chemical and physical vapour deposition and electrodeposition. Clearly each of the three processes has its own advantages and disadvantages but most researchers tend to regard electrodeposition as the most simple and flexible of the three. It is therefore this technique which will be reviewed in this investigation.

CMMC Electrodeposition Techniques

Electrodeposition can be utilised in broadly two ways to produce CMMCs:

- The dual dath technique (DBT)
- The single bath technique (SBT)

In the first technique the substrate is repeatedly transferred between two electrolytes, each depositing a particular single metal or alloy. The DBT also requires careful rinsing techniques before each deposition step. This usually involves normal rinsing in water following deposition and then in the following electrolyte before the deposition stage for the next layer. This elaborate format is required to try and limit cross electrolyte contamination and passivation of the freshly electrodeposited metal surface. Clearly there are drawbacks with the DBT, however, it is relatively simple and does allow the deposition of alternate layers of pure metals, a situation which is difficult to achieve with the SBT. The SBT technique, by definition, is less cumbersome to operate but has a far more complex electrolyte chemistry. The single electrolyte contains both metallic species to be deposited, the conditions for successful deposition have been summarised by Despic and Jovic [3]:

- The two metals to be electrodeposited must have different standard and electrodeposition potentials. This is so that the more noble of the two metals can be deposited for the desired period of time (thickness) without deposition of the more base metal.
- The concentration of the more noble metal must be at a sufficiently low level to enable the more base metal to be electrodeposited at a high cathodic potential.
- The re-dissolution of the more base metal by anodic processes, when the potential is returned to the value to deposit the more noble metal, must be sufficiently slow. This must occur to let the base metal remain intact until it is covered by a layer of the more noble metal.

The nature of the SBT means that the substrate remains in the electrolyte continually with potential or current be used to bring about the formation of the different layers. There is therefore no chance of passivation causing problems. The main drawbacks with this technique are the difficulties associated with producing pure metal layers and the consequential need for fine current (or potential) control, often achieved via a potentiostat/galvanostat or by controlled pulse electrodeposition.

Historical Development Of CMMCS
One of the earliest references to multilayer coatings was made by Brenner and Pommer [4] who produced a multilayer Cu-Bi alloy from a single electrolyte. The layered structure was utilised as a diffraction grating after suitable etching. Cohen et al [5] reported the production of Ag-Pd structures from a concentrated chloride bath, individual layer thicknesses were produced to values below 50 nm and the coating properties were seen to include reduced electrical resistivity and increased tarnish resistance. A large number of investigators have examined the Cu-Ni multilayer system. This metal pairing was one of Koehler's favoured systems and lends itself to relatively easy electrodeposition both in the DBT and SBT formats. Investigators therefore found that this system was useful in examining the potential attributes of CMMCs, particularly electrodeposition methods and the ability to reduce individual layer thicknesses to less than 5 nm [6-8]. More recent investigations have examined the use of the Cu-Ni system for giant magnetoresistance.

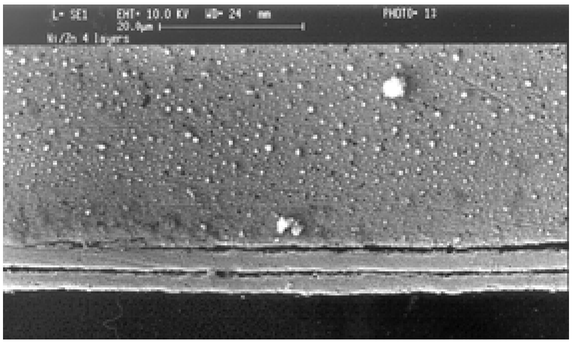
Corrosion Protection By Zinc-Based CMMCS
In reality the research into CMMCs can be divided into levels, basically dependent on the final application of the coating system. Many electrical and electronic uses require very small individual layer thicknesses, often as low as a few nanaometres. Whereas corrosion resistance and wear minimisation require larger overall coating thicknesses and hence individual layers of the order of microns.

Many of the CMMCs investigated for corrosion protection have been based upon electrodeposited zinc alloys, with the sacrificial protection of ferrous substrates as the end goal. Investigators at Loughborough University have been particularly interested in this class of multilayer coating.

Zinc-nickel based CMMCs
Baral and Maxmovitch [9] were one of the first investigators to examine this particular system. They operated a dual bath configuration depositing successive layers of zinc and nickel with individual layer thicknesses of 20-500 nm using a rotating disc electrode.

Kalantary et al [10] carried out a feasibility study into the electrodeposition of CMMC of zinc-nickel alloys onto mild steel rotating cylinder electrodes (RCEs). The RCE format allows a controlled turbulent agitation regime to be utilised for the formation of coatings. A single bath sulphate-based electrolyte was used to produce the coatings, with electrode rotation speed and current density being utilised to form different coating structures and compositions. A wide range of electrodeposition conditions brought about a variety of coating formats. This data was then utilised to produce the first simple multilayered structures. Three individual coating layers were deposited at current densities of 1, 10 and 100 A/dm^2. Metallographic cross-sections produced the evidence for the three individual layers and subsequent neutral salt spray corrosion tests suggested good corrosion performance. Further work by the same authors [11] concentrated on examining the morphology of the Zn-Ni CMMCs and importantly, their corrosion resistance. A range of CMMCs (all nominally 8μm overall coating thickness) were corrosion tested in sodium chloride solution and salt fog along side zinc and zinc-nickel alloy monolithic coatings of a similar thickness. In essence, the layered structures were shown to have the superior corrosion resistance. For duplex zinc-nickel alloy coatings it was found that the more noble layer (higher nickel content) should be adjacent to the surface. Kalantary et al [12] also attempted to obtain corrosion data using a polarisation technique. Eight and sixteen layer coatings nominally of 8μm total coating thickness were examined by cathodic and anodic polarisation in 3.5% NaCl solution. Overall curve shapes were similar although measurement of corrosion currents suggested that the corrosion rates for the eight layer structures were higher.

Chawa et al also [13] used individual zinc and nickel baths to electrodeposit CMMCs on mild steel substrates, photograph 1 illustrates a simple four layer structure electrodeposited on to mild steel.



Photograph 1 Four layer nickel-zinc structure electrodeposited onto a mild steel substrate from a dual bath configuration

A further advance with this system was to utilise a zinc-nickel alloy electroplating bath so that layered structures of Zn-Ni/Zn and Zn-Ni/Ni could be deposited [13]. A sulphate-based bath was used to electrodeposit the zinc, a sulphamate formulation for the nickel and a proprietary bath for the zinc-nickel alloy which gave a nickel content of approximately 12%. To obtain successful CMMC deposition for zinc and nickel layers the authors suggested that:

- When electrodepositing nickel onto zinc the current should be raised slowly to the desired level
- Agitation had to be concentrated below the cathode.

Corrosion protection capabilities were also assessed using both neutral salt fog tests and electrochemical trials using the anodic Tafel extrapolation method. Important findings can be summarised as follows:

- The upper nickel layers on zinc were relatively porous
- The upper zinc layers on nickel were relatively pore-free
- Corrosion currents suggested, in general, that layered structures reduced coating activity
- Four and eight layer Zn-Ni/Zn (zinc being the uppermost layer) had times to red rust in the salt spray trials that exceeded monolithic Zn-Ni coatings by approximately 200 hrs.

Table 1 illustrates corrosion resisting trends of layered and monolithic coatings.

Kalantary et al [14] also examined a dual bath zinc/nickel system based on sulphate electrolytes. Using similar experimental techniques to Chawa they again showed the

Coating type*	Number of individual layers	E_{corr} mV vs SCE	Hours to 5% red rust in NSS
Zn	1	-1060	197
Ni	1	-450	71
Fe	-	-610	-
Zn/Ni	4	-735	223
Zn/Ni	8	-1005	179
Ni/Zn	4	-1050	336
Ni/Zn	8	-1035	324
Zn-12% Ni	1	-996	313
Zn/Zn-Ni	4	-1030	329
Zn/Zn-Ni	8	-1040	287
Zn-Ni/Zn	4	-1020	552
Zn-Ni/Zn	8	-1080	519
Zn-Ni/Ni	4	-660	208
Zn-Ni/Ni	8	-670	181
Ni/Zn-Ni	4	-980	328
Ni/Zn-Ni	8	-900	276

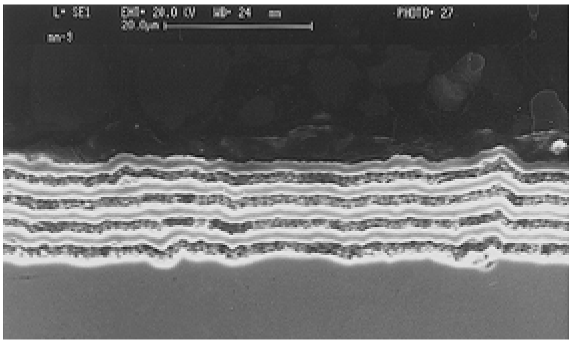
** For multilayer coatings of repeating X/Y, Y represents the top layer*

Table 1 Corrosion resistance results for substrate, single and multilayer coatings

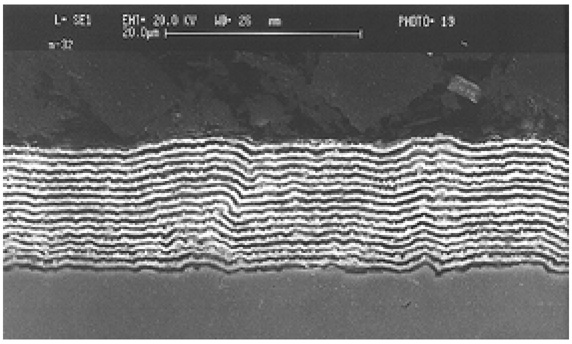
advantages of the CMMC structures, although in contrast to Chawa's work they found thinner individual layers promoted better corrosion resistance properties.

Zinc-Iron Based CMMCs

Electrodeposited zinc-iron alloys have found considerable use as sacrificial coatings for ferrous metal surfaces. It is therefore only proper that they be examined for their ability to form multilayer coatings on the same type of substrate. To this end Liao et al [15-17] have examined both single and dual bath zinc/zinc-iron and zinc-iron only systems. Photographs 2 and 3 illustrate 9 and 32 layer Zn/Zn-Fe structures electrodeposited onto a mild steel substrate by a dual bath technique. Experimentation was sequential in nature with initial studies examining the effect of electrodeposition current density and solution hydrodynamics using a rotating hull cell designed by Madore and Landolt [18]. Using a combination of various rotation speeds and current densities this particular Zn-Fe system was found to be eminently suitable for CMMC production. Also examined was the addition of ammonium chloride as a conductivity salt which improved the quality of the electrodeposits produced. In a second series of investigations, Liao et al examined the morphological-controlling aspects of the current density and agitation level [16]. Again a rotating Hull cell was utilised. Current density was found to have the greatest effect on electrodeposit morphology and compositions of less than 1 wt% and 15-75 wt% produced a fine crystal structure. Once the electrodeposition parameters were fully assessed CMMC structures were produced from the single electrolyte [17]. Additives such as citric acid, thiourea, polyglycol and sodium acetate were utilised to ensure level individual layers.



Photograph 2 Nine layer Zn/Zn-Fe CMMC electrodeposited onto a mild steel substrate from a dual bath configuration



Photograph 3 Thirty two layer Zn/Zn-Fe CMMC electrodeposited onto a mild steel substrate from a dual bath configuration

Jensen et al improved the zinc –iron CMMC system proposed and first utilised by Liao et al [19,20]. The main improvements were the addition of ascorbic acid as a reducing agent and the use of mild steel as an anode material. Further additives were used to ensure level, coherent individual layers. The improved zinc-iron formulation was ideal for CMMC production because of the two plateaux on the composition-current density plot. Thus a single bath system could alternate between the two current density levels to produce the required CMMC structure. A second single bath Zn-Fe system was employed to produce CMMC structures under high speed electrodeposition conditions.

Zinc-Cobalt Based CMMCs

Until recently the zinc-cobalt alloy system was probably one of the least investigated zinc alloy systems for the production of CMMCs. Probably some of the most noteworthy investigations have been carried out by Kirilova et al [21-23]. Initial investigations were carried out to produce one and two-layer structures from both dual and single baths [21]. Greater numbers of layers were also electrodeposited using dual and single baths [22]. Anodic stripping voltammetry was utilised as the technique with which to examine these structures. For both dual and single bath structures, the dissolution of the coatings occurred at more positive potentials than for zinc but more negative than cobalt. For both dual and single bath systems, the greater the number of overall layers the more positive the dissolution potential. A third series of investigations by Kirilova et al [23] examined the corrosion resistance of Zn-Co alloy CMMC structures. Corrosion potential measurements and conventional neutral salt spray corrosion tests were carried out. The corrosion potentials of single bath structures were found to have a more positive potential than their dual bath counterparts. Neutral salt spray tests suggested the best resistance to white corrosion product was exhibited by a four layer single bath specimen of 12 μm overall coating thickness and in a chromated condition. In general layered structures with a top layer of Zn, Co or Zn-Co1% showed no red rust even after 1584 hours of testing. Similarly it was found that for the same overall coating thickness a small number of layers (in this case 4 against 40) produces the best corrosion resistance.

More recently Bahorololoom et al have examined Zn-Co CMMC structures, but with much higher cobalt contents [24]. They found that electrolyte solution reactions had a big effect on cobalt content. More specifically the production of Co^{3+} ions by anodic oxidation had a deleterious effect on obtaining high cobalt contents in the electrodeposits. It was found that a divided cell was required to allow cobalt to remain in the divalent oxidation state at the cathode surface. It was also found that the divided cell allowed the electrodeposition process to operate as an equilibrium mechanism as opposed to an anomalous one which was found for the single compartment cell. Zn-Co deposits, obtained from the two-compartment cell, were found to regularly contain cobalt at levels over 70% at appropriate current densities.

Zinc-Manganese Based Multilayers

Of the main zinc alloys successfully electrodeposited, zinc-manganese, is the one which has yet to make its mark commercially [25]. It has been suggested that it could well be an effective sacrificial coating on steel for a number of applications such as steel strip [26] and wire [27] although it is unlikely to have gained any significant industrial status due to its inherent difficulties in electrodeposition. The main electrolyte utilised by investigators has been the sulphate-citrate formulation. This zinc-manganese electrodeposition suffers from two main drawbacks:

- Poor cathode current efficiency, often as low as 30%.

- Poor electrolyte stability resulting in the precipitation of manganese (III) citrate.

With these inherent difficulties with the main zinc-manganese electrolyte (sulphate-citrate) it is not surprising to find that very little effort has been made to electrodeposit Zn-Mn CMMCs on ferrous substrates. Nitipanyawong et al have attempted to produce Zn-Mn layered coatings from a single sulphate-citrate bath [28]. Structures containing 4-50 individual layers have been successfully produced using current density as the composition control.

Conclusions

This short review has highlighted the status of layered or CMMCs. It is clear that there are several end-uses for such structures. One of these is for the barrier and sacrificial protection of ferrous surfaces. This as been achieved through the deposition of zinc alloy CMMCs. A series of zinc alloys have been utilised in this way and a number of the systems are showing promise.

The future, therefore, looks very good for this type of coating, not only in its zinc-based sacrificial role, but also many of its others. Many electrodeposited alloy systems have yet to be examined and utilised in the CMMC format, this will, in all probability, occur in many cases over the next few years. Other CMMC themes are also areas where interesting advances can be made. One of these is with graded coatings. The possibilities of producing a coating with each component of an electrodeposited alloy varying through the coating has very interesting possibilities. Another area of note for the future is layered composite coatings. There is some recent work reported on this [29], but as with graded coatings, its potential has not been fully investigated.

References

1. Gabe D R. Principles of Metal Surface Treatment and Protection, 2nd Edition, Pergamon Press, Oxford, p86 (1978).
2. Koehler J S. Phys. Rev. B, Vol 2, P547 (1970).
3. Despic A R and Jovic V D. J. Electrochem. Soc., Vol 134, P3004 (1987).
4. Brenner A. Electrodeposition of Alloys. Principles and Practice Vol II, Academic Press, New York, P589 (1963).
5. Cohen U, Koch FB, Sard R. Electrochemical Society Meeting, Orlando, USA (1981).
6. Benette L H, Swatzendruber L J, Lashmore D S, Oberle R, Atzmony U, Dariel M P, Watson R E. Phys. Rev. B., Vol 40, P4633 (1989).
7. Roos C A, Goldman L M, Spaepen F. J. Electrochem. Soc. Vol 140, P9 (1993).
8. Haseeb A, Celis J P, Roos J R. J. Electrochem. Soc. Vol 141, P230 (1994).
9. Barral G, Maximovitch S. Colloque de Physique, Vol 51, No 14, PC4-291 (1990).
10. Kalantary, M R, Wilcox G D, Gabe D R. Electrochimica Acta, Vol 40, P1609 (1995).
11. Kalantary M R, Wilcox G D, Gabe D R . Proceedings of UK Corrosion 95, 21-23rd November, 1995, Harrogate, UK.
12. Kalantary, M R, Wilcox G D, Gabe D R in Advances in Surface Engineering. Volume II: Process Technology, Edts Datta P K, Burnell-Gray J S, Royal Society of Chemistry, P265 (1997).
13. Chawa G, Wilcox G D, Gabe D R. Trans. Inst. Met. Fin. Vol 76, P117 (1998).
14. Kalantary M R, Wilcox G D, Gabe D R. Br. Corros. J. Vol 33, P197 (1998).

15. Liao Y, Gabe D R and Wilcox G D. Plat. & Surf. Fin. Vol 85, No 3, P60 (1998).
16. Liao Y, Gabe D R and Wilcox G D. Plat. & Surf. Fin. Vol 85, No 8, P62 (1998).
17. Liao Y, Gabe D R and Wilcox G D. Plat. & Surf. Fin. Vol 85, No 9, P88 (1998).
18. Madore C, Landolt D. Plat. & Surf. Fin. Vol 80, No 11, P73 (1993).
19. Jensen J D, Critchlow G W, Gabe D R. Trans. Inst. Met. Fin. Vol 76, P187 (1998).
20. Jensen J D, Gabe D R, Wilcox G D. Surf. & Coat. Technol. Vol 105, P240 (1998).
21. Kirilova I, Ivanov I, Rashkov St. J. Appl. Electrochem. Vol 28, P637 (1998).
22. Kirilova I, Ivanov I, Rashkov St. J. Appl. Electrochem. Vol 28, P1359 (1998).
23. Kirilova I, J. Appl. Electrochem. Vol 29, P1133 (1999).
24. Bahoroloom E, Gabe D R, Wilcox G D. Submitted to J. Electrochem. Soc (2002).
25. Wilcox G D, Petersen B. Trans. Inst. Met. Fin. Vol 74, P115 (1996).
26. Sagiyama M, Urakawa T, Adaniya T, Hara T, Fukuda Y. Plat. & Surf. Fin. Vol 74, No 11, P77 (1987).
27. Bozzini B, Pavan F, Bollini G, Cavallotti P L. Trans. Inst. Met. Fin. Vol 75, P175 (1997).
28. Nitipanyawong C, Wilcox G D, Gabe D R. Proceedings of SURFIN 2000, Chicago, USA.
29. Kerr C, Barker D, Walsh F, Archer J. Trans. Inst. Met. Fin. Vol 78, P171 (2000).