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Electrodeposited Multilayer Coating Systems

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Abstract

The use of multilayered electrodeposits, to enhance coating performance especially in corrosive environments, has uncertain origins but has been systematically practiced and optimized since the 1950s.

The background to such systems will be traced, examples given of their usage, and the recent development of nanometre multilayers by pulsed plating techniques described.

1. INTRODUCTION

The purpose of underlayers is to make conventional electrodeposition both possible and functional/protective on a normally more base (ie. active) metal surface.

The development of coating composites, systems or layered structures cannot easily be traced to an origin but has grown from early recognition of the need to optimize a number of properties from adhesion to substrate to minimization of surface tarnishing. The earliest deposition practice was to use thick coatings to achieve longevity of service with cost met by use of substitute materials, eg. silver substituting for gold. The first underlayers were employed as a means of improving brightness through buffing of the substrate (before solution brighteners were common) : hence the use of copper under nickel and nickel under silver and gold (nb. duplex nickel systems date from the 1950s and depend entirely on the use of additives). Parallels can be found in ancient times where cladding and gilding required intermediate layers, often of mercury, to ensure good adhesion or bonding through diffusive alloying. Similarly, the necessity of using primer, underlayer and topcoats of paint is very old practice.

A number of pretreatments have become part of the customary technology and include what is usually termed strikes. Two examples may be cited ; firstly the use of cyanide copper solution to 'strike' a first layer on zinc substrates which is successful because of the strongly complexed nature of the cyanide solution. Secondly, the use

of a chemical immersion-type deposit on aluminium (or other very base metal like titanium), often zincate or stannate, prior to the electrodeposition of copper or nickel.

The current preferred term is for a sequence of layers on a substrate is system because composite has a separate usage (particles or fibres layed in a matrix). The subject has been discussed previously[1] and three types can be distinguished (see Fig. 1):

1) Overlays deliberately formed in sequence.

2) An underlayer produced by interdiffusion either during a hot process or by post treatment.

3) A post treatment, in its simplest form a passivating dip.

Some layered structures were formed accidentally or incidentally (typically hot-dipped alloy layers) and it is probably only in the 1950s that layered systems in general were recognized as worthy of optimization. Three well-established examples (corresponding to the above three categories) are as follows.

1) The use of Ni underlayers for Cr to yield corrosion protection and decorative finishes-the names of Knapp, Brown, Safranek, Du Rose come to mind.

2) The use of flow-melting in electrolytic tin_2 plate production to yield a thin continuous alloy layer of $FeSn_2$ to promote superior corrosion performance of cans containing corrosive foods.

3) The use of chromate or phosphate passivation treatments on electrodeposits of Zn and Sn to promote tarnish/oxidation resistance and lacquer/paint adhesion.

Such layers tend to be in the thickness range of 1-20㎛. The recent (1990s) concept of multilayers is to produce a sequence of layers 《1 ㎛ thick which can enhance a variety of physical, as well as chemical, properties, eg. magnetic memory ability in ferromagnetics including Cu-Ni alloys. For practical reasons these need to be produced in one solution using pulsed currents which cause layers of different composition to be deposited. The alternative route of PVD or CVD is known and used for ceramic materials and base metals but is not competitive for metals and alloys capable of being electrodeposited from aqueous solutions. In the earlier paper[1] a few examples were discussed. It is proposed that other examples will be described here which lead into the options offered by pulsed current techniques. Such other examples do not necessarily relate to corrosion and examples will be described in which tribological advantage and diffusion barriers are attained.

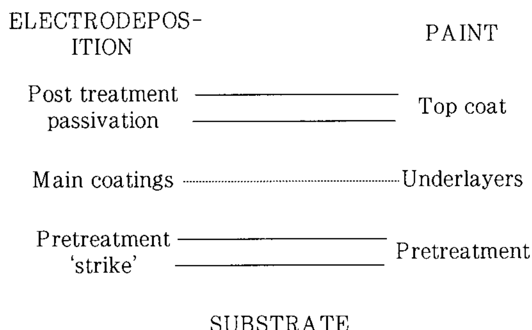


Fig. 1 Illustrated terminology of pre- and post-treatment layers.

2. THE NICKEL PROBLEM.

Nickel has been used for many years as an underlayer for thin or vulnerable topcoats. A

number of examples can be listed but two will be considered here. Firstly, the use of nickel under chromium, a topcoat which is vulnerable by virtue of its tendency to crack when deposited bright and stressed. Thick chromium has not been considered for corrosion resistance and decorative applications since 1945 when underlayers were first studied in depth with the automobile industry in mind. Amongst many studies those of Knapp may be considered typical: he tested inumerable combinations involving nickel as underlayer and toplayer with further underlayers of Sn, Zn, Ag, Pb, Pd, Cu, Fe etc. The conclusions led towards the dull Ni-bright Ni-Cr system eventually formalized as BS 1224 (ISO 1456) which was explored previously[1]. This is still widely used today and can be summarized as follows:

CONDITIONS	NICKEL UNDERLAYER	CHROMIUM TOPLAYER
4. Very severe outdoors	40㎛ duplex	0.3㎛ R
	30㎛ duplex	0.3㎛ M
3. Normal outdoors	40㎛ bright	0.3㎛ R
	30㎛ bright	0.3㎛ M
	30㎛ duplex	0.3㎛ R
	25㎛ duplex	0.3㎛ M
2. Indoors with humidity	20㎛ bright or duplex	0.3㎛ R or M
1. Indoors dry	10㎛ bright or duplex	0.3㎛ R or M

Duplex = dull nickel + bright nickel
R = regular chromium
M = microdiscontinuous chromium

The difference between using thinner and thicker underlayers of nickel is illustrated in Fig. 2.

Secondly, the use of nickel under gold as a protection underlayer largely because of the need to minimize the thickness of gold in non-professional electrical applications and for

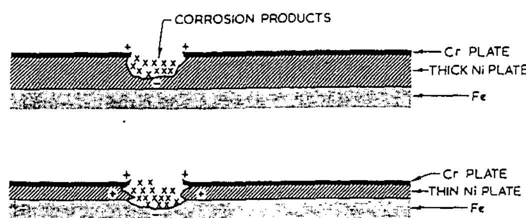


Fig. 2 Duplex Cr-Ni layered coating on steel showing corrosion with thin and thick nickel underlayers.

cheaper ranges of jewellery and related products. Here the substrate may be copper or steel, the nickel is used at 5-15㎛ thickness and the gold is purely cosmetic at 0.2-1.5㎛ thickness. Until recently, this was sound scientific and economic practice. However, skin allergies have now been recognized which can be attributed to nickel and at 1㎛ thickness gold has sufficient porosity to allow the allergy to be actvated by skin contact with jewellery once sensitization has taken place (usually through previous blood contacts, eg. ear-piercing). While the statistics of such allergy suggests that it is not a major or life-threatening problem it is seriously unpredictable; consequently the replacement of nickel is considerd desirable. A number of alternatives have been enumerated; for example, Simon and Puippe[3] have separately suggested-

Bronzes which can be white, hard (>400VPN) and tarnish-resistant (55%Cu-45%Sn), or yellow, hard and less corrosion resistant (80%Cu-17.5%Sn-2.5%Zn).

Proprietory versions are available as Miralloy (Degussa) and Optalloy (Fluhmann).

Palladium which is white, ductile and crack-free, and can be used in principle as a gold replacement also if the colour change is acceptable.

What is unclear is how nickel alloys can be considered because Pd-Ni is a well-established electrodeposit and the implications for the use of austenitic stainless steels containing 8-10% Ni is potentially serious, eg. cutlery.

The implications may have other far-reaching aspects because many alloy golds (used at lower caratage for hardness and cheapness) may contain nickel in which case alternatives such as Co, Zn, Fe etc must be specified. Furthermore, gilding baths may also require change.

3. DIFFUSION BARRIER LAYERS.

Diffusion can be induced through elevated temperature treatments to promote coating/substrate adhesion and this is a recognized means of creating internal underlayers. However, such diffusion can be undesirable if it diminishes properties which are matters of priority. Several examples may be cited and Kay and Mackay[4] were amongst those who identified important characteristics, in their case for diffusion between tin and brass or copper (see Fig. 3). Three consideratio-ns were investigated for which diffusion barrier layers would be desirable:

1) the need to maintain a 'free' tin surface layer on components to retain good solderability,

2) the need to minimize selective diffusion fron an alloy substrate, eg. zinc from brass, which would reduce solderability,

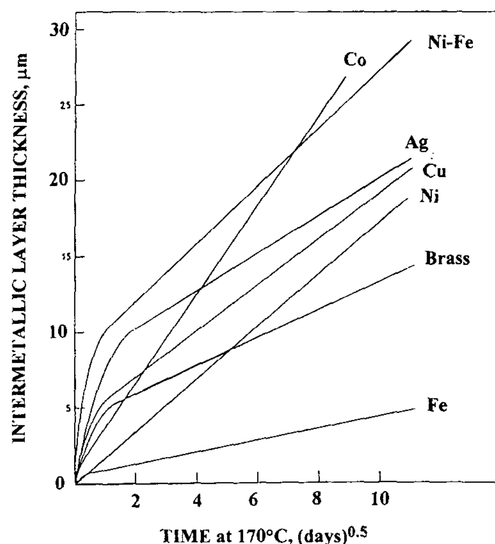


Fig. 3 Intermetallic compound thickness for tin on various barrier layers after diffusion at 170℃ (after Kay and MacKay).

3) to minimize alloy layer growth of intermetallic compounds which would increase interface brittleness.

A large number of electrodeposit options were investigated-Sn-Ni alloy, Cu-Sn 'speculum', Pb, Ni, Co, Fe, Ni-Fe and on the basis of a criterion of400 days at 170℃ iron was regarded as a best option. A not unrelated problem concerns the minimization of tin whisker growth on electronic components and connectors during storage which can lead to short-circuits opportunities when used. Underlayers of Pb can act as diffusion barriers in this case[5, 7]. Clearly, the diffusive behaviour must be established and for tin the behaviour of a number of options are illustrated in Fig. 3.

Gold coatings suffer from change of colour due to diffusion effects and barriers are an important aspect of their specification. The situation is complicated by the fact that alloy golds

are widely used to provide adequate wear and a variety of substrates may be involved. The traditional diffusion barrier has been nickel with nickel-palladium (20-25% Ni) being an established alternative[8]. The concern over nickel has led to further alternatives being sought of which palladium-iron (20-25% Fe) has received some attention[9-11]. Other options have been investigated by Chow[11] and include Cu-Pd, Cu-Pd-Fe, Cu-Co, Cu-Co-W; diffusion results suggest that Co-W may be good but no commercial standard practice has emerged yet.

Underlayers for ceramic gold plated packages are a related application: essentially the production of metallized conductor tracks on ceramic packages for semi-conductor mounts. A nickel underlayer is usually used to suppress the gold/silicon eutectic reaction and consequent creation of Kirkendall voids which lead to serious loss of die bond strength. Examples of their practical specification are:

Original specification:	3.2㎛ Ni+5㎛ Au
Superior specifications:	3.2㎛ Co or Ni-Co alloy
	0.2㎛ Co+3㎛ Ni
	3㎛ Pd or Rh

These layered structures minimize diffusion through the nickel during annealing at 700℃. Diffusional alloy layers up to 40㎛ thick can develop which may consist of Ni_2Si with the Au-Si eutectic. Further nickel diffusion through the outer gold layer under conditions of high temperature oxidation (eg. 400℃) yields a surface film of NiO which reduces contact quality and wettability[12, 13]. This shown in Fig. 4.

Nickel underlayers typically exhibit substantial amounts of nickel on the gold surface, ie. ~ 25%. If the nickel underlayer contains 10-40% there is a significant reduction in nickel level at the surface, typically 9~10%. Examination of the diffusion data suggests that there is probably no virtue in using more than 12-15% cobalt in practice (Fig. 5).

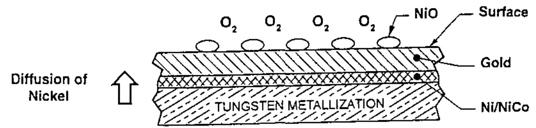


Fig. 4 Nickel underlayers for gold on ceramic packages.

Other examples can be cited, the most notable being the use of Pt and Y on jet engine turbine blades to minimize the diffusion-controlled oxidation and aluminide growth of nickel-based alloys.

The use of alloy elements and barrier layers to control alloy layer growth on hot dipping is well-established and has long been commercial. However, the need to provide control in 'galvannealing' is a driving force. One example is the use of oxide layers on Fe in a Zn-Fe reaction to inhibit initial rapid growth.

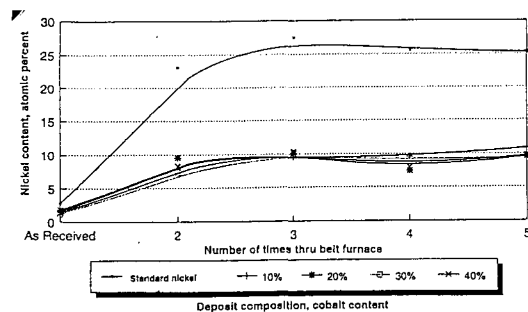


Fig. 5 Use of nickel layers under gold, showing that the presence of 10-15% Co in Ni is a substantial diffusion inhibitor.

4. LEAD ALLOY BEARING SURFACES.

Electrodeposited lead alloys represent the most widely used group of soft metals used for engine bearings[14]. They provide a superior conformable oil (hydrodynamically) lubricated material for both internal combustion and Diesel engines, remaining stable for long periods of engine usage. The properties required include the following:

- Fatigue strength : oscillatory loads at high temperature
- compressive strength : loading without dimensional change
- embeddibility : tolerate foreign matter and minimize consequent wear.
- conformability : tolerate misalignment, eccentricity etc.
- compatibility : minimize seizure
- corrosion resistance : resist attack by acid oil additives and degradation products.

A number of overlay coating materials can be considered for selection. The usual basis is a steel shell with a clad copper covering. An alternative is an aluminium shell with nickel electroplate after special pretreatment (eg. Bondal) to remove preformed oxides and promote good adhesion. Overlays then include Lead-tin (5-12% Sn) ; Lead-tin-copper (10% Sn, 2% Cu) ; Lead-indium (5-10% In) all in the 'as electrodeposited' condition. Alternatively, indium on lead on copper followed by a diffusional treatment is also used.

Structural limitations have been identified in that tin can diffuse to the copper layer and form a brittle intermetallic compound[5] An under-layer of nickel (1-3㎛) acts as a barrier to such formation and incorporation of copper in the overlay inhibits the diffusion process. But bond strength decreases as the Ni-Sn layer thickens so it is not without disadvantage. Indium is known to offer superior properties which have been assumed to be associated with surface lubricity.

A number of new layered formats have been proposed amongst which as a new concept is an attempt to eliminate tin from the overlay, which thereby removes any necessity for a nickel barrier layer and also eliminates the need for having copper in a ternary alloy electrodeposit. Therefore, although indium is more expensive, by depositing it directly on lead and diffusion treating it a viable overlay can be produced.

Typically, lead (20㎛) is electrodeposited on the clad copper steel shell followed by indium (3-8㎛). This is subject to 0.5-2 hours at 155℃ when indium diffuses inwards (see Fig. 6) to form an In-Cu alloy layer consisting of δ-Cu_7In_3 which contains

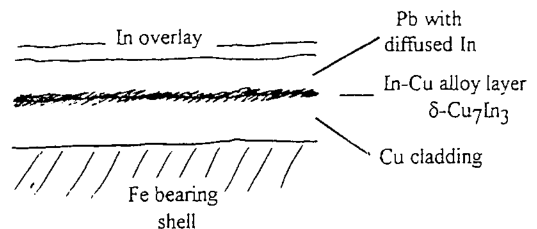
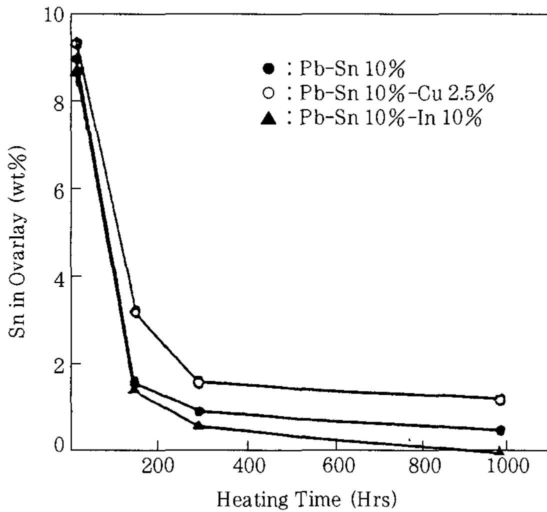
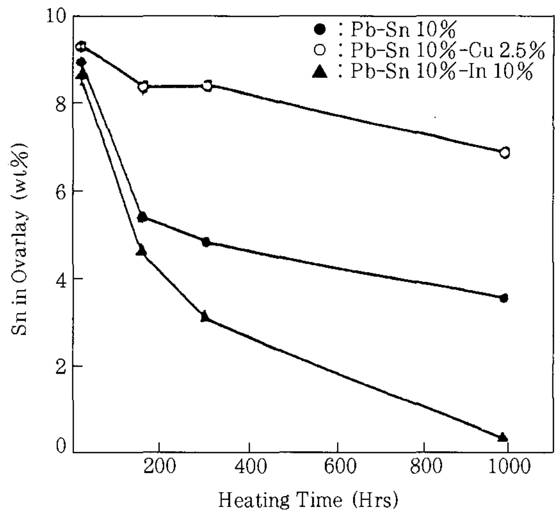


Fig. 6 Use of underlayers for In overlays on copper-clad steel bearing shells.

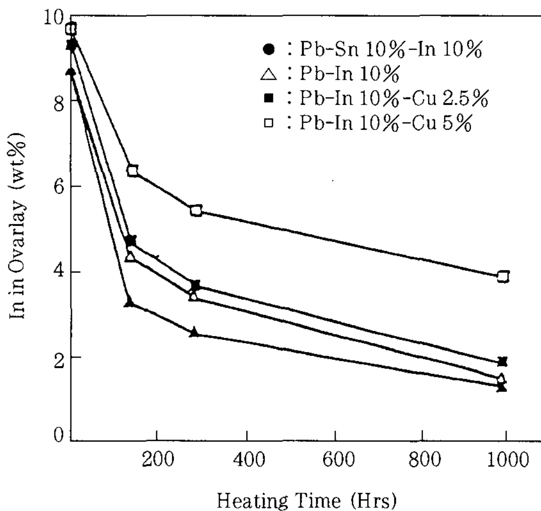
30 at % In[16]. Figs. 7a, b show the effect of nickel barrier layers (1.5㎛) on the diffusion of tin. In the absence of nickel tin diffuses into the substrate very quickly, an effect reduced by the presence of copper. Figs. 7c, d show that for in-



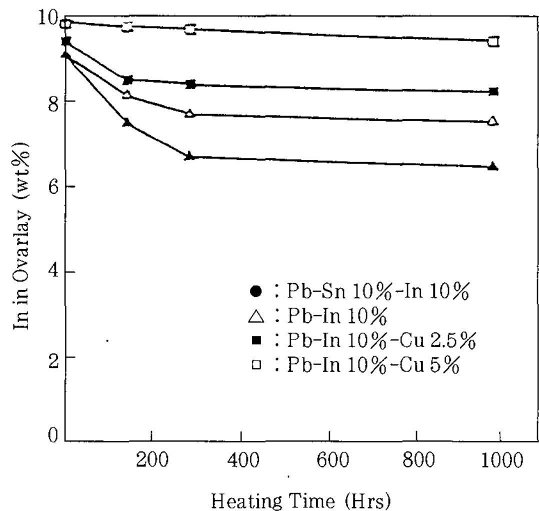
Tin Content Retaining in Overlay after Heating at 165°C; without Nickel Barrier on Cu-Pb 25% Alloy
(a)



Tin Content Retaining in Overlay after Heating at 165°C; with 1.5㎛ Nickel Barrier on Cu-Pb 25% Alloy
(b)



Indium Content Retaining in Overlay after Heating at 165°C; without Nickel Barrier on Cu-Pb 25% Alloy
(c)



Indium Content Retaining in Overlay after Heating at 165°C; with 15㎛ Nickel Barrier on Cu-Pb 25% Alloy
(d)

Fig. 7 Data for indium bearings using underlayers and diffusional treatments.

dium the rate is lower than for tin and the presence of nickel makes it even slower.

A schematic cross-section of the bearing structure after production or on initial usage is shown in Fig. 8. Detailed analysis of the diffusion process and resulting structures has been carried out using Electron Probe Microanalysis and EDAX techniques.

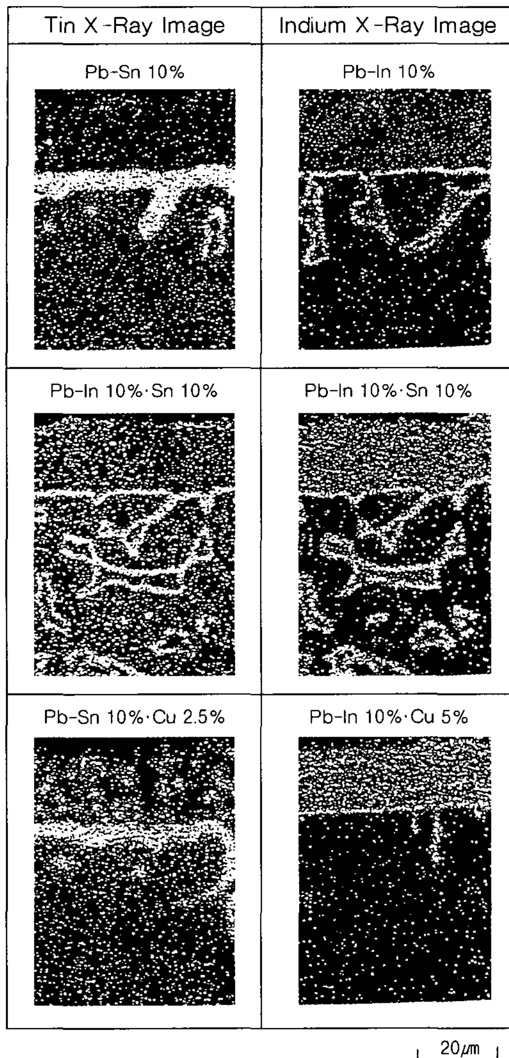


Fig. 8 EPMA X-ray micrographs after 1000hr. heat treatment. No Ni barrier on a Cu-25%Pb alloy.

5. STRUCTURE MODULATION.

By structure modulation we usually mean the change of surface topography rather than change of crystal structure so as to modify the surface reactivity in the context of roughness, adsorption or adhesion. Crystal structure modulation is not yet common and only a few examples have been noted. For example:

- Chromium: hexagonal CrH decomposes to bcc Cr with a 15% shrinkage. It is effected by current pulsing and recrystallization; hydrogen evolution leads to a reduction of hardness and brittleness.
- Cobalt.: hcp Co is produced with a low rate of polarization caused by slow pulsing and fcc Co with a high rate of polarization and fast pulsing. The magnetic properties are most affected.

A well-established application of structural modulation exists in the case of electroformed copper foil for Printed Circuit Boards. Here it is common to specify a smooth outer surface for soldering and a rough inner surface for enhanced adhesive bonding to the insulative polymer baseboard.

Electroforming is carried out from acid copper electroplating solutions on to a stainless steel drum (the former) which is slowly rotated.

- A smooth surface is produced adjacent to the former using an initial low c.d., high agitation and high process temperature.
- A rough surface is produced adjacent to the solution using a high c.d., low agitation and low process temperature.

A typical solution formulation is Cu 35-120g/l+H_2SO_4 75-120g/l. Deposition conditions are:

low c.d. 20-90 A/dm^2 at 55-65℃

high c.d. 100-400 A/dm^2 at 65-75℃

The bond strengths reported are typically in the ranges (see also Fig. 9):

Smooth surface	0.35-0.90 kg/cm
Improved surface	.40-1.80 kg/cm

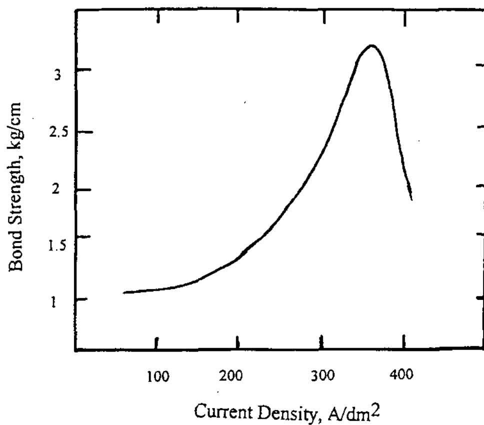


Fig. 9 Bond strengths to electroformed copper foil.

Superior surface 2.60-3.0 kg/cm

A number of enhancing post-treatments, designed to stabilize or lock rough surfaces and provide cohesion to any powdery/dendritic deposits, have been patented[17] and include

- smooth copper over rough copper [17e]
- zinc or brass flash over rough copper [17e,g]
- nickel flash over powdery copper [17d]
- chromate flash over copper powder or CuO nodular surface [17f]

6. COMPOSITION MODULATION BY CURRENT PULSING.

The concept of multilayer electrodeposits produced by composition modulation of alloy plating solutions is often attributed to Blum in 1921 and Brenner in 1949 who proposed either the use of two solution or one solution and current switching from one level to another. More recently, current pulsing was used by Yahalom, Lashmore, Celis and others to produce very thin layers which could exhibit marked enhancement of certain physical and mechanical properties. Such enhancement was predicted by Koehler in 1970 and a number of theoretical models exist to explain this behaviour-see Gabe and Green[18] who quote the references mentioned. Because Cu-Ni solutions are ideal for this purpose much work has been reported for this alloy but other alloys are now being explored.

The principles are simple and have been defined by Despic (see Appendix). An alloy solution is designed so that by pulsing from low to high current (agitation may also be changed) the alloy deposit composition is changed and by further designing the Faradaic charge It passed layer thickness can be planned and controlled. In principle, therefore, nanolayers can be produced using pulses <1s in duration. In order to ensure layer uniformity the morphology must be understood and maintained at a levelling character. Such layers are termed Composition Modulated Alloys (CMA).

It is anticipated that much research will be concentrated in this area and some advances can be expected in the next few years. One such opportunity-zinc alloys-is discussed in the next section.

7. DUPLEX ZINC ALLOY COATINGS.

The object of duplex zinc alloy coatings is to provide improved corrosion performance when the alloys are electrodeposited in layers of differing composition. Ideally the process would utilize one solution and two different current densities but historically two solutions have been used for practical reasons. Passivation with chromating or phosphating usually enhances the effect. Examples include Zn-Ni and Zn-Fe.

In the case of Zn-Ni alloys a typical solution having a good %Ni vs CD relationship (see Fig. 10) for producing duplex (CMA-type) electrodeposited coating would be:

$ZnSO_4$	100-300g/l
$NiSO_4$	300-400g/l
Ni/Zn ratio	1-4
Total thickness	10㎛

The two layers would have the following format:

First layer	20A/dm^2	5㎛	9%Ni
Second layer	5	5	5%Ni

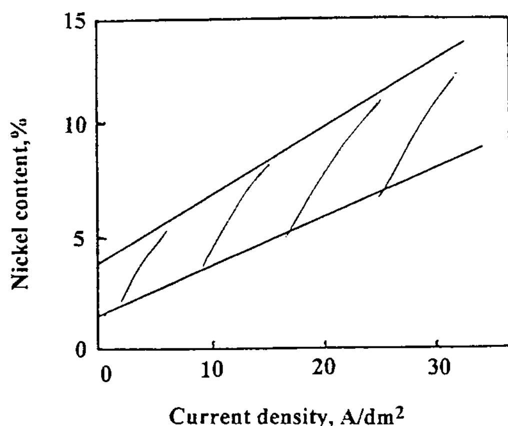


Fig. 10 Typical relationship between %Ni and current density for a Zn-Ni alloy solution.

The coatings remain sacrificial to steel with up to 15-18%Ni. By using a duplex structure an improved corrosion performance from 500 to 1000 hours to red rust appearance has been claimed. This represents a relatively minor compositional difference and Kalantary, Gabe and Wilcox[19] have explored the limits of this type of layering.

Of the various electrodeposited zinc alloys, only Zn-Fe has been considered to any great extent over a number of years as a multi-layered coating. The proposed scheme consists of two layers:

First layer	20g/m^2 (6-10㎛)	10-20%Fe	galvanic protection of steel
Second layer	3g/m^2 (1-2㎛)	75-80%Fe	good phosphating capability for painti-nt adhesion.
Third layer	1g/m^2 (0.5㎛)		phosphate layer

The two layers have been produced commercially by the use of two successive solutions with composition and pH adjusted to provide the two deposit compositions. The Japanese process[20] uses ferrous-zinc sulphate containing sodium sulphate as conductivity salt and sodium acetate as complexant to stabilize Fe_2^+ ions. The solution is then anomalous in behaviour as zinc deposits preferentially. A preferred solution composition is:

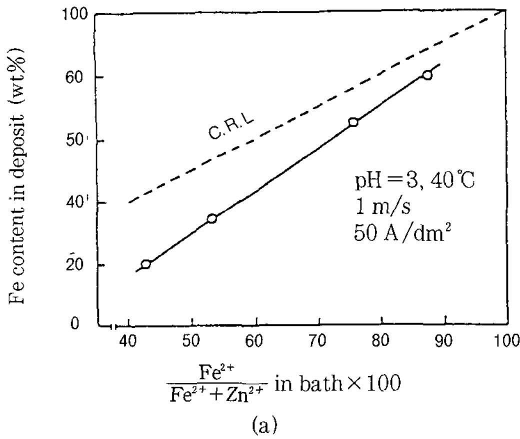
$FeSO_4+ZnSO_4$	500g/l
$Na2SO_4$	30g/l
CH_3COONa	20g/l
$C_6H_8O_7$	5g/l

Deposit composition can be varied through four main parameters (see Fig. 11):

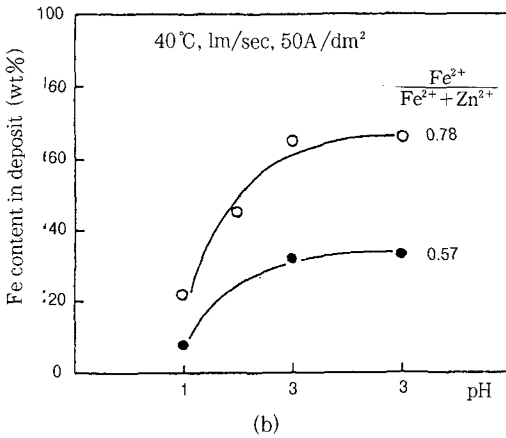
1. metal ratio
2. pH
3. flow rate
4. current density.

In order to maintain solution conductivity the total metal content is held at 500g/l but the ratio of one metal to the other is varied. The two composition targets are easily attained. However, the pH can only be varied in conjunction with the metal ratio.

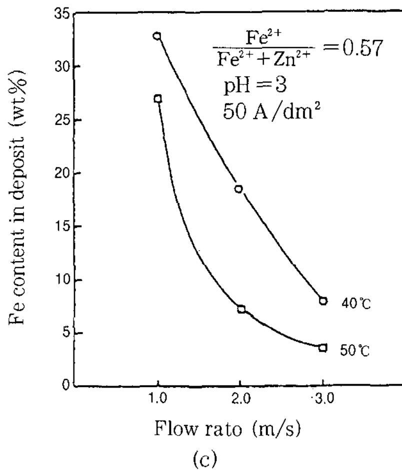
Flow rate enhancement can be achieved with a jet nozzle flow superimposed upon the contin-



(a)



(b)



(c)

Fig. 11 Fe content of Zn-Fe alloy deposits as a function of three main process parameters.

uous strip or sheet movement. Its main use is to ensure uniformity of composition within a narrow range.

Current density variation provides a systematic change in alloy composition but probably inadequately for good product control for two preferred compositions without substantial optimization being undertaken.

An improved solution for CMA production has been developed by Gabe and coworkers[21-23] and exploits the ability of chloride to modify the mechanism of deposition from equilibrium to anomolous thereby giving much more flexible control of deposit composition through the usual process parameters of current density and agitation.

The mechanism of corrosion of such a coating is governed not by the 'classical' potential gradient but by the presence of a paint and phosphate top coating system as the primary coating protection. The use of an iron-rich layer on the outside of the alloy layered system is only justified by the over-riding need of a good phosphate film because it itself is not particularly corrosion resistant.

Many sacrificial coatings can exhibit a passive tendency and thermodynamically a range of oxide-type compounds can be cited as possible corrosion products. In practice their relevance depends upon the existence of chloride traces in the environment which limits their stability.

It appears that Zn-Fe, Zn-Ni and Zn-Co alloys do not form such films and in any case they are normally used at 'optimum' compositions where they remain active and unpassivated (ie. anodic and sacrificial) towards iron. In the case of Zn-Mn, however, the exceptional corrosion

resistance for an otherwise more active alloy does suggest that a passive film of predominantly γ-MnO.OH can form.

A little explored but related aspect is the possibility of potential reversals occurring after long periods of galvanic corrosion; this is evidenced by slow shifts in corrosion potential with time (see Fig. 12). The explanation is found in recognizing two stages of behaviour:

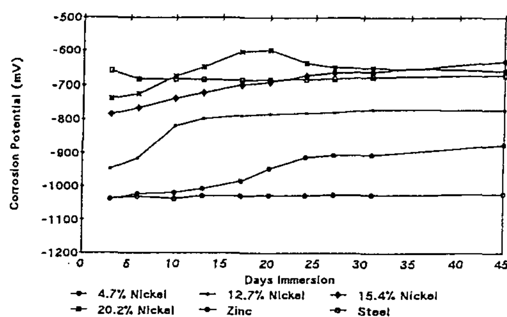


Fig. 12 Corrosion potential of four Zn-Ni alloys with time; Zn and steel potential values as reference lines.

1) initial selective dissolution of zinc leaving a nickel enriched surface;

2) at approximately 25%Ni the alloy undoubtedly becomes more noble than ironnd reversal occurs leading to loss of galvanic (sacrificial) protection.

When painted the corrosion behaviour can be substantially modified due to the presence of both phosphating pretreatments and the paint system which itself may consist of primer, undercoat and topcoat. Thus properties such as corrosion resistance and paint adhesion will depend upon alloy composition in entirely different ways and ultimate choice of preferred will necessarily be a compromise.

<50%Fe in Zn: good paint adhesion but poor corrosion resistance.

>50%Fe in Zn: good corrosion resistance but poor paint adhesion.

8. CONCLUSIONS

Electrodeposited multilayered coating systems have been known for many years but their development has been substantially on an ad hoc basis. The behaviour is now more fully understood in a number of types of application and the range of thicknesses possible varies from the nanometre level to many micrometres in the case of long term corrosion and wear prevention.

It should now be possible, perhaps by using established examples, to design multilayers once the performance type and service requirements are adequately defined.

REFERENCES

1. D. R. Gabe. Electrochim Acta 1994, 39, 115.
2. R. R. Knapp. Trans. IMF 1958, 35, 139.
3. F. Simon. Proc Asia-Pacific Interfinish Congress, Melbourne, 1994, 1, 15-1;J. Cl. Puippe. Trans IMF 1992, 108.
4. P. J. Kay and C. A. Mackay. Trans IMF 1979, 57, 169.
5. K. G. Compton, A. Mendizza and S. M. Arnold. Corrosion, 1951, 7, 327.
6. S. C. Britton. Trans. IMF 1974, 52, 95.
7. M. Jordon. The electrodeposition of tin and its alloys, Eugen G.Leuze, Saulgau, 1995.
8. E. J. Kudrak, J. A. Abys, V. Chinchankar

and J. J. Maisano. Plating Surf. Fin. 1992, 79(2), 49.
9. P. Juzikis, M.U.Kittel and Chr.J.Raub. Plating Surf. Fin. 1994, 81(8), 59.
10. M. E. Baumgartner. Ph. D. Thesis, Loughborough University, 1998.
11. a. K. M. Chow. M. Phil. Thesis, Hong Kong Polytechnic University, 1997.
b. K. M.Chow, W. Y. Ng and L K.Yeung. Surf. Coat. Technol. 1998, 99, 161.
12. J. S. Russo. Plating and Surface Finishing 1994, 81(7), 63.
13. Shinichi Wakabayashi et al. ibid 1994, 81 (11), 58.
14. D. R. Eastham and C. S. Crooks. Trans.Inst. Met. Fin. 1982, 60, 9.
15. N. A. Kermali and D. R. Gabe. Surface Technol. 1982, 15, 1.
16. M. Sakamoto, M. Wada and Y. Ogita. S. A. E. Tech. paper M1,1989 Congress, Detroit.
17. Patents for structural modulation of electroformed copper foil:
   a. USP 3 220 897 Conley et al principles defined
   b. USP 3 328 275 Waterbury ditto
   c. USP 3 674 356 Yates ditto
   d. BP 1 211 494 Yates nickel flash
   e. BP 1 349 696 Yates copper, zinc or brass locking flash
   f. BP 1 328 319 Yates chromate locking and antistain
   g. BP1 293 801 Clevite brass, zinc, indium on surface of nodular copper
   h. BP 1 293 802 Clevite ditto
18. D. R. Gabe and W. A. Green. Surf. Coating Technol. 1998,
19. M.R. Kalantary, G. D. Wilcox and D. R. Gabe. Electrochim Acta 1994, 40, 1609.
20. T Adaniya, T. Hara, M. Sagiyama, T. Homa and T. Watanabe. Plating Surf. Fin. 1985, 72, 52.
21. Liao Yongzhong, J. D. Jensen, G. D. Wilcox and D. R. Gabe. Proc SURFIN Conf., Minneapolis, June 1998.
22. J. D. Jensen, G. D. Wilcox and D. R. Gabe. Surf. Coating Technol. 1998
23. J. D. Jensen, G. W. Critchlow and D. R. Gabe. Proc EUROFIN Conf., Brighton, 1998.

APPENDIX

DESPIC'S CRITERIA FOR CMA DEPOSITION FROM A SINGLE ELECTRODEPOSITION SOLUTION.

1. The two metals constituting alternating layers must have sufficiently different dynamic potentials ($E^\circ + \eta$) so that the more noble metal (M_1) can be deposited for a desired time without deposition of the more active metal (M_2).
2. The concentration of metal M_1 must be sufficiently low so that raising the cathodic overpotential (η) would cause total limiting current conditions to prevail thereby enabling metal M_2 to deposit.
3. Redissolution of metal M_2 by anodic reaction, when the potential is returned to that for metal M_1 to deposit, must be sufficiently slow so that metal M_2 remains undissolved until it is protected by the new layer of metal M_1.