CRITICAL REVIEW ON
ALLOY PLATING: A VIABLE ALTERNATIVE TO
CONVENTIONAL PLATING

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Conventional metal plating is becoming insufficient to meet many of the recent technological demands. Deposits with new properties are to be tailor made to cater the needs of the computer age. New alloy electrodeposits are being explored with different motives such as improving properties, material conservation, environmental/health safety and producing products at affordable cost besides miniaturization. Reports are available on numerous alloys which is difficult to be accommodated here. Hence, only commercially successfull new processes are presented in this review.

Keywords: Alloys, zinc, tin, cadmium replacement, chromium alternative, gold substitute.

INTRODUCTION

Electroplating technology is responding in both revolutionary and evolutionary ways to a number of significant driving forces. These include the need to meet new technological requirements for both existing and new applications. The stimulus for this change is to achieve higher levels of productivity based on quality, increased production rate and lower cost. Often, it is in response to an external threat such as competitive technology or a new environmental regulation. Presently there has been increasing concern about the effluent of industrial chemical discharges on the environment. Some of the more toxic and dangerous chemicals include cyanides, hexavalent chromium and several other halogenated solvents. Yet another area of concern is the escalation in the price of noble metals viz., gold for applications in electrical and electronic industry which dictates the development of suitable alternatives to economise the use of gold in these area.

Alloy plating offers better solutions for many of the plating problems faced today with respect to environmental safety and economic viability. Some of the alloy which have been a commercial reality in these days, as alternatives to cadmium, chromium and gold, the most widely used metals in the trade, are discussed in this article.

Zinc alloys

Introduced over fifteen years back as a means of improving the corrosion resistance of zinc, electrodeposited zinc, alloy coatings have achieved an important position in the protection of ferrous substrates throughout the world [1]. Zinc alloys can be easily designed electrochemically to produce different corrosion potentials, to maintain the sacrificial protection of zinc at a slower dissolution rate. Some of these alloys are excellent replacement to cadmium in many applications [2,3].

Extensive investigation in various parts of the world have shown marked improvement in corrosion resistance over zinc, especially for zinc alloyed with nickel, cobalt, iron and manganese. Today the alloys have been proved to be commercially successful in automotive [4], aerospace [5] and even in construction industry [6].

Zinc-cobalt

The earliest system to be introduced as an alternative to conventional zinc plating was zinc-cobalt deposited from an acid electrolyte containing additives since, it offered easy possibility of conversion from a conventional neutral chloride zinc bath or non-cyanide zincate bath [7] with suitable complexants and additives [8,9]. The alkaline bath has the advantage of producing almost same alloy composition with current density which enables less

composition dispersion on irregular shaped cathodes thus increasing the protective value of the coating [10-17]. With cobalt content in the range of 0.6-1.0% and with yellow, bronze and black chromate finishes [11,18], the system finds application mostly in automotive parts, including those made of high strength steel and cast iron components [19,20]. Research on non-chromate treatments based on $CeCl_3/H_2O_2$ have also received current interest [21].

When zinc cobalt alloys corrodes, cobalt promotes a corrosion product in the form of a complex salt. This film is comparatively compact and stable and its electrical conductivity being poor, inhibits corrosion effectively. During corrosion, since zinc dissolves in preference to cobalt, the alloy will be enriched internally and forms a layer to slow down corrosion [22]. Zinc-Cobalt alloy is corrosion resistant in atmospheres containing sulphur also and shows excellent results [8,20,23,24] in the Kesternich test [19]. But, its overall corrosion resistance to red rusting is less than that of zinc-nickel [24]. As a replacement to cadmium plating [25], this coating is also used in luxury cars and equipments used for oil and gas exploration. It is also suitable for barrel plating of small components [2,19].

A recent report claims that zinc-cobalt is better suited to develop a bond between rubber and steel in the manufacture of vehicle tyres [25,26]. Currently use of brass coating promote bond but, deteriorate with time due to corrosion of underlying steel [26,27]. Zinc-Cobalt (with < 1.0 wt% cobalt), used as a replacement of brass, promote adhesive strength as that of brass and prevents red rust formation which increases service life of automobile tyres compared to brass [27].

Recently, compositionally modulated zinc-cobalt alloys are receiving interest [28]. The best corrosion resistance so far reported with regard to the appearance of white rust was observed for the compositionally modulated multilayers (CMM), chromated for 20 seconds and consisting of four sublayers each 3 μm thick, deposited from a single bath where the overlayer is zinc-cobalt (1%). The corrosion resistance of coating deposited from a single bath is better than of coating deposited from a dual bath. For CMM with an over sublayer of Zn, Co or Zn-Co1%, no red rust appears on the surface even after 1584 hrs of salt spray test. Their corrosion resistance with regard to the appearance of white and red rust is much better than that of pure Zn or Zn-Co (0.8%) alloys.

Zinc-nickel

Enormous amount of literature is available on the production and properties of this system [29-32]. Two different systems are available to produce this alloy, acidic [33-35] and alkaline non-cyanide [36-39], both capable of producing deposits of exceptional corrosion resistance with the nickel content ranging from 10-14% in the former and 5-9% in the latter. Normally ammonium chloride is used for the acid electrolyte [40-43] and organic complexing agents are used for the alkaline electrolyte [44,45].

The alkaline baths have the advantage of uniform nickel content in deposits at low and high current densities [1]. Another advantage is its non-corrosive nature to unplated internal areas. It is better in terms of corrosion resistance [46], ease of operation and range of applications including cadmium replacement [46-48]. It is a stable bath both for rack and barrel plating [48]. However, the carbon content of the deposits caused by the brightener used, should be controlled within limits as it induces brittleness in the coating. The complexants chosen should not lead to any problem during waste disposal [46-48].

The acid bath is more efficient, but produces high nickel at low current densities [49], affecting chromating as well as sacrificial protection in these areas. Hence, it is recommended more for strip plating and in electrical transmission industry. The effluent problem associated with the use of ammonium chloride [40,50] in a plating bath has driven some suppliers to develop processes based on boric or acetic acid [1]. The alloy is used in combination with iridescent, yellow, deep bronze and black conversion coatings [20]. Special chromate passivation treatment solutions are required as those available for zinc tend to produce a black finish due to the presence of the alloying element in the deposit [51,52]. The extended neutral salt spray test requires 768 hrs to red rusting for 8 μm thick Zn-Ni with iridescent chromium and with bronze chromate 1000-1200 hrs to red rust. Just like cadmium, Zn-Ni plated parts are easily chromated after baking with minimum activation [13]. Another advantage of chromated Zn-Ni over zinc and cadmium is its ability to maintain a high corrosion resistance following heat treatment [20].

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wax system (b) silicate based systems and (c) lacquer coatings are used widely to reduce the adverse effects of heat treatment [56]. The microcracked nature of the zinc alloy indicated it as a suitable candidate to replace cadmium on high strength steel [57-61]. While the micro structure is normally lamellar, when the alloy is deposited, the stress levels cause microcracking to occur [57-64].

The problem of hydrogen embrittlement is more likely to occur in alkaline zinc-nickel than in acid due to much lower current efficiency (60%) [59]. Hydrogen can be absorbed into the base metal during plating. But, matte deposits from microcracked net work in the alloy which allow hydrogen path through the electroplates facilitating its escape and preventing the coating acting as a dense, embrittling blanket layer preventing egress of hydrogen [59-64]. The microcracking also contributes to the excellent corrosion resistance, stabilising a barrier of corrosion products at the coating surface held in a matrix of non-corroded nickel that acts as a controlling barrier [51].

Inclusion of phosphorous along with Zn-Ni alloy is found to improve the corrosion resistance of the alloy [65,66]. Recently, these alloys have been found suitable even for the construction industry [6].

Zinc-iron

Mostly acid type processes based on sulphate or chloride based with citric acid as the complexing agent [67,68] are used. These electrolytes are used for strip plating at 50 A.dm^{-2} [69]. Though more difficult to plate than zinc-nickel alloy, zinc-iron alloy has good phosphatability and paintability [70], the two weaknesses of zinc-nickel alloy [67]. Excellent workability and corrosion resistance are achieved in the range of 15-25% iron and good paintability above 50% [69]. Hence, a dual layer alloys, the first layer containing around 18% iron and the top layer containing around 80% iron are considered beneficial to combine the above properties with good corrosion protection. Close control of hydrodynamic conditions are considered essential to achieve alloy composition homogenity in steel [70] which probably leads to a very uniform chromate layer formation showing optimum corrosion resistance in the salt spray test even after a preceding heat treatment. Zinc deposits containing 0.5-1.0% iron, produced from alkaline non-cyanide baths, often high levels of corrosion besides their ability to produce highly adherent good quality chromate coating including non-silver containing black coatings. This system is generally chosen since it is economical, simple

to install and effluent treat and produce low concentration silver free black coatings [69-71].

The degree of corrosion protection offered by these alloys is less than that of zinc-nickel but, better than zinc [4]. Ternary alloy system containing iron and cobalt has been recently introduced in Japan [1]. Produced from an alkaline non-cyanide electrolyte with appropriate additives to yield bright, ductile and non-stressed coatings [38], the deposit with the alloying elements' content ranging from 0.25-0.5% functions both as a good base for chromate passivation [71] and possess good corrosion resistance offered by codeposited iron and cobalt respectively [46]. Applications of Zn-Fe include, fuel system components such as fuel rails, automotive and non-automotive fasteners, chassis components and door latch hardware [10,18,38].

Zinc-manganese

Bearing in mind the cost factor, various other alloy systems have been developed [38]. One that shows promise is Zn-Mn which is deposited from a sulphate-citrate bath [72-76], with potassium bromide to improve bath stability. Although the corrosion potentials of these alloys containing 40% manganese was similar to zinc, under salt spray conditions they show nearly 1.5-2.5 times better corrosion resistance than zinc [77,78]. Its corrosion resistance is superior to both zinc and zinc alloys in chloride environment. The main problem over its commercial utilisation is due to its low current efficiency and poor bath stability. It is possible to draw Zn-Mn (13-40%) coated wires even though the hardness of the coating gives some problem. The drawing performance can be improved by plating an external layer of zinc on Zn- Mn alloy deposit [79]. More details on zinc alloys are given in Tables I-III.

Tin alloys

Tin metal possesses many desired properties such as corrosion resistance, brightness, conductivity, solderability, lubricity etc., by which it finds application both in decorative and electronic industry [67]. Tin based alloy deposits (Pb-Sn,Sn-Bi,Sn-Co,Sn-Ni) [80] are widely used instead of precious metals viz., gold, in preparing electronic devices, printed circuit boards and for soldering purposes. Recent reports indicate that they are better suited to replace the hazardous metal deposits such as cadmium and chromium.

TABLE I: Zinc alloys — overview [19]

	Zn-Co		Zn-Fe	Zn-Ni		Zn-Sn
	Acid	Alkaline		Acid	Alkaline	
Alloying element	0.4-1.0%	0.4-1.0%	0.3-1.0%	7-13%	4-7%	70-80%
Electrolyte	Pot chloride Amm chloride	Caustic	Caustic	Amm chloride	Caustic	Neutral
C.C.E.	95-100% 50-80%	50-80%	90-95%	30-50%	90-100%	
T.P.	Poor	Good	Good	Poor	Good	Good
C.C.C.	Y,D,B	Y,D,B	Y,B	Y,D	Y,D	Y

C.C.E. = Cathode efficiency; T.P. = Throwing power; C.C.C. = Chromate conversion coatings available
Y = Yellow; D = Drab and B = Black

Tin-zinc

An alloy containing 70-80% tin offers the best protection for steel. [81-83]. This alloy combines the protective value of tin with the sacrificial nature of zinc and does not form the typical white corrosion product seen with the zinc electroplate [84,85]. The best protection is offered by 70% tin alloy. The chromated alloy gives 2500 hours resistance to salt spray by which these alloy are discussed as the best substitute to cadmium in the coastal and industrial climates.

This alloy is deposited from four different electrolytes viz., acid, alkaline cyanide, alkaline non-cyanide and neutral [81]. The acid type bath operates at pH 1.0 with tin-zinc anodes and contains about 1.0% zinc. Chromate conversion coatings are difficult. The alkaline cyanide and noncyanide baths deposit 70-80% tin and easily accept chromate conversion coatings. These baths should be heated to 343 K and their anodes must be electrolytically filmed similar to stannate tin baths. The neutral baths with the above characteristics are found suitable in rack and barrel conditions [86,87]. The anodes need not be filmed as tin is present only in the divalent state. Other electrolytes are based on gluconates, diphosphate, fluoborate EDTA and so on.

The adhesion of the chromate films is superior to those of zinc [83,84]. This is largely due to the anchor function of the second metal to zinc [85]. The chromated tin-zinc deposits excel in corrosion protection even after the part is bent, crimped or deformed which can be possible due to the softness of the deposits. The alloy has very good conductivity in the chromated form [86,87]. Tin-zinc

alloys appear to out-perform other zinc alloys in the Kesternich test [19].

They show very good solderability that exceeds those of cadmium and zinc [88-90]. The deposit's good solderability [91,92] even after ageing is a good attribute which makes it a suitable alternative to tin-lead solder deposits [93]. These deposits do not form whisker growth even after 600 days. Devoid of tin pest formation at low temperatures, these coatings are not microcracked. Tin-zinc offers good protection of steel-aluminum contacts [94]. Friction and wear characteristics are good and deposit resists contact with break fluid or gas line [95]. It has been reported that these alloys exhibit EMI/RFI shielding properties. The hydrogen embrittlement is relieved by heat treatment at 463 K for 4 hours [95]. The deposits are not microcracked as are other deposits. This technology is considered to be the most suitable one having properties similar to cadmium and is receiving much attention in USA and UK [96].

Tin-zinc alloys are used in hydraulic parts, joining elements, welding bolts, switches, aircraft and automotive parts, electronic chassis and electrical engineering. They are also potential replacement to tin-lead layers [83,84,93,97].

Tin-copper and tin-copper-zinc

During the last few years the use of electro-plated nickel for some decorative applications such as fashion jewellery, accessories, watches etc, which are typically coated with a nickel deposit to avoid the diffusion of the base material through the top layer eg, gold [97-99] is receiving much concern. If nickel comes in direct contact with human skin, approximately 20% of women and 5% of men

develop skin allergy. To avoid exposures to allergic nickel a number of countries have taken measures to establish a cost effective alternative to nickel viz., copper-tin or copper-tin-zinc alloy.

Depending on the alloy composition either yellow or white coloured deposits can be produced. While coloured deposits contain 55% copper and 45% tin or 55% copper 30% tin and 15% zinc, the yellow deposits contain 80% copper 17.5% tin and 2.5% zinc [94]. Processes are available for both rack and barrel plating. The process utilises an alkaline cyanide-stannate bath [100]. The use of insoluble anodes is an essential tool to control the metal concentration of the bath. These alloys are characterised by an excellent distribution of the layer thickness due to the alkaline nature of the bath [88] and can be easily overplated. They show an acceptable solderability [81,95] and are diamagnetic which is an important pre-requisite for the plating of connectors in the telecommunication field. The excellent corrosion resistance of the alloys on copper substrates is also used in the automotive industry, their excellent tarnish resistance makes them a viable substitute to silver in the decorative applications and their high hardness and solderability even after storage [100,101] is utilised as a substitute for tin especially in electronic field.

Tin-nickel and Tin-Cobalt

Tin-nickel alloy electrodeposits have been commercially established over many years and are characterised by good corrosion resistance hardness, lubricity and attractive appearance [103]. Electrodeposited tin-nickel is an example of an alloy with properties that are not the average of the properties of the elements. Since this alloy does not contain free nickel, it is much less likely to cause nickel induced allergic reaction and hence is a potential substitute to pure nickel in skin contact applications for example jewellery, watches, bracelets etc., [102].

In hardness, tarnish resistance and resistance to chemical reagents, it far excels both nickel and tin [91]. Although hard and brittle and somewhat subject to impact damage, thin coatings (2-3 μm thickness) can be deformed without flaking [103,104]. The coatings do not tarnish easily even in nitric acid vapour and in atmospheres containing sulphur-di-oxide and hydrogen sulphide nor they are susceptible to whisker growth [105]. The wear resistance is good and does not have any undesirable magnetic properties. Sn-Ni coatings finds application as an etch resist on printed circuit boards because of their resistance to strong acids and as a low cost contact layer under gold on connectors [106]. Contact resistance is stable over a period of time. Freshly deposited coatings can be soldered easily. Sn-Ni alloys are used in fuse caps, lugs, coaxial cable connectors, magnetic memory tapes (with a rhodium overlay), connectors and electrical switch gear. Application temperature is limited to 623 K, above which decomposition of the intermetallic compound occurs [107]. The system can be applied for both rack and barrel plating and for decorative and functional applications.

Fluoride based acid baths [107] and complex based alkaline baths [108] are widely used. Alternative electrolytes based on pyrophosphate, triethanolamine /hydrochloric acid have also been reported. The amine bath operates at neutral pH and low temperatures. Alloy

TABLE II: Neutral salt spray corrosion resistance [19]
(0.3 mil thickness), hours

Chromate	Sn-Zn		Zn		Alk. Zn-Co		Alk. Zn-Fe		Zn-Ni	
	FWC	FRR	FWC	FRR	FWC	FRR	FWC	FRR	FWC	FRR
Blue bright			24	48-72	24-30	72	24-30	72		
						120		120		
Yellow	150	1000	60	160	220	500	220	500	300	700
			120	250	480	700	480	700	400	900
Oilve drab			96	350					800	1200
			150	450					1000	1500
Black (Ag)			48-72	160	48	100	48	160		
				300	120	350	120	350		
Black (non-Ag)			240	600	240	600				
			500	800	800	800				

TABLE III: Properties of Zn alloys [19]

Alloy	1	2	3
Zn-Co	Better than Zn	100-125	0.23
Zn-Fe	Equal to Zn	80-130	0.28
Zn-Ni, acid	Equal to Zn	140-160	0.34
Zn-Ni, alk	-Do-	260-310	—
Zn-Sn	Better than Zn-Co	13-17	0.23

1 = Kesternich results; 2 = Hardness VK50
3 = Friction factor

compositions are remarkably stable over a wide current density range in acid and alkaline baths and has covering power and throwing power equal to cyanide copper and stannate tin. Hardness is 650 VHN which falls in between bright nickel and chromium. The alloy has exceptional chemical resistance and is cathodic to steel and anodic to nickel.

Sn-Ni alloy has a slightly pinkish hue compared to chromium, whereas Sn-Co obtained from an acid bath has a blue colour nearest to the shade of chromium [109]. The cobalt alloy has a hardness of 300-400 VHN and hence, soft compared to chromium [110]. These alloys basically designed to replace hazardous chromium have already partly replaced the latter in the industry. The disadvantages inherent in chromium plating such as poor current efficiency and throwing power, high energy costs and corrosive and toxic electrolyte not suited for barrel plating etc., [111,112], promoted the introduction of this process as an alternative to the former in the industry and even in brush plating [94]. The colour of the deposit, although not identical to chromium, is probably close enough not to cause adverse comments and is by far the closest of the available alternatives to hexavalent chromium electroplating processes [109,110].

Precious metal alloys

The driving force for gold substitution in industry is its cost on one hand and on the other, its increasing demand in the electronic age. From children's' toys to luxury cars, everywhere electronics has spread its wings and to add, the present day miniaturization of components warrants suitable alternatives to gold just to reduce the cost of the components at a much affordable price.

Palladium-nickel

In the past decade, the electronic industry has been seriously investigating the use of palladium and palladium- nickel alloy electrodeposits as contact materials

[113]. With a flash of gold they are better wearing than conventional hard gold. The thin overplate of gold has the added advantage of protecting the alloy surface from the atmosphere [114-116], thereby maintaining low stable contact resistance between mating surfaces. The alloy produced excellent ductility and relatively high elongation without cracking. The hydrogen contents of the alloy is very much lower than pure palladium. Other advantages are, low resistance to finger printing, lower density and lack of catalytic activity. It is increasingly being used in connectors, PCB industry, semiconductor applications etc., [114-119].

The major problem posed by palladium-nickel alloy is the difficulty to estimate its composition and thickness which is primarily an issue of quality control [120]. Further, it has been found that this alloy is thermally stable only up to 398 K making it unreliable for high temperature applications. Therefore, there is a need to develop an alternative alloy which would exhibit many of the positive attributes of Pd-Ni alloy and yet to overcome its deficiencies. Palladium-Cobalt [121] is the recently developed alternative to Pd-Ni, possessing higher hardness and wear resistance than the former. The quality control issue of measuring the composition and thickness of the Pd-Ni can be easily resolved with Pd-Co [122-123].

Palladium-silver

The diffusion of gold into wrought palladium-Silver alloys led to the introduction of a new series of inlays which have been qualified for modern high reliability connector applications. The reported advantage of these palladium-silver composites over their palladium- nickel counterparts is their ability to withstand fretting corrosion. Recent research has resulted in the development of viable electrolytes capable of producing functional palladium-silver electrodeposits. Although still in its infancy, the use of electrodeposited palladium-silver alloy is expected to grow in conjunction with other palladium based system to meet the ever increasing technological and cost demands of the electronic industry [123].

CONCLUSION

Alloy plating is an emerging area which can cater numerous industrial and engineering needs. Applications are ever increasing and more are yet to be explored. The modern computer applications depends more on alloy depositions as thin films. With the growing modernisation on instrumental techniques and quality control, alloy deposition is no more a difficult job as indicated by the

number of processes which have become commercial success.

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