RECENT DEVELOPMENTS IN ELECTROPLATING, 1960-1964

PART I METALS

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ABSTRACT

The electrodeposition of metals and binary alloys has been reviewed with special reference to plating baths, general techniques and applications.

INTRODUCTION

THE science and art of electroplating have made rapid strides during the last 25 years. The experience gained during the last war has led to significant developments in the plating industry. Research work in this field has also contributed towards progress from the theoretical as well as practical view-point. The recent trends in electroplating are: plating from new types of baths, role of addition agents, bright plating, alloy plating, precious metal plating, plating on uncommon bases and non-conductors, production of deposits with special properties, applications as in electroforming and aerospace, and studies on the structure of deposits, throwing power of plating solutions and polarization phenomena. The post-war work has been reviewed in two papers from this laboratory[1,2]. This paper outlines the developments in single metal deposition during the period 1960-1964. Alloy plating will be covered in a subsequent communication. Ternary alloy deposition has been recently reported in detail elsewhere[3]. A comprehensive review is not attempted, the object being chiefly to bring out the highlights.

PLATING OF METALS

Nickel:

A large amount of work has been done on the plating of nickel, and the scope is expected to expand during the coming years since the metal is no longer in shortage today. Various types of baths have been used: perchlorate[4], sulphate[5], fluoride[6]; complext salt baths like cyclohexylethylenediaminetriacetic acid[7], oxalate[8] and pyrophosphate[9-12]. The nickel ammonium sulphate solution[5] gave bright deposits without any addition agents. Saccharin, coumarin, tellurium, selenium and arsenic were used as brighteners for the phyrophosphate bath[10].

Electrolytic black nickel coatings have been found to be more corrosion resistant than other black oxide coatings[13]. The sulphate-chloride bath with naphthalene disulphonic acid gave bright nickel deposits on copper, the brightness being evaluated by reflectivity and microhardness[14]. A similar bath has been found to be satisfactory for the plating of plastics[15]. Zinc and its alloys have been nickel plated direct from sulphate-chloride solutions containing EDTA, 2-mercaptobenzimidazole and saccharin[16]. Several processes have been described for plating on uncommon bases to meet specialized requirements: sulphate[17], and fluoborate[18,19] solutions for aluminium; sulphamate for beryllium[20]; sulphate[21] and chloride with some additions[22] for titanium; and a bath free from boric acid for uranium[23]. An evaluation has been made on the use of nickel plating of thorium and uranium components for improving the bond obtained by soldering[24].

Copper:

Amongst acid baths for copper plating, mention may be made of the perchlorate[25] and sulphamate[26,27] types. Brighteners like gelatin, glue, EDTA and sulphosalicylic acid have been found to increase the cathode polarization during deposition from sulphamate solutions[27]. Further developments have been reported on copper plating from the pyrophosphate bath: effect of the ultrasonic field and PRC[28]; addition of hydrolyzed gelatin and glycine for bright plating[11]; deposition in two steps with low and high concentration baths for good adhesion and high quality plating[29]; direct plating on zinc base die-castings with solutions containing dimercaptothiadiazole as additive[30]. Other baths include amines-ethylene diamine[31-33] and ethanolamine[33], and cyclohexyl

EDTA[7]. The deposits from the ethylenediamine bath were dense and fine-grained, with a microhardness of 140-150 Kg/mm^2. They retained the original brightness to a thickness of 20μ and did not tarnish after months of exposure to air[32]. The amine complex solution also gave bright plates[33].

The pyrophosphate bath has also been mentioned as suitable for plating on uranium[34], steel wire[35] and aluminium[36], and the sulphate bath for molybdenum and tungsten[37]. Bright deposits have been obtained on steel from sulphate solutions containing thiourea[11]. A bath containing copper carbonate, sodium sulphate and disodium EDTA has been described for plating on steel or iron either for protecting areas during cementation or as an interlayer for further decorative, multilayer electroplating[38].

Chromium:

Conditions have been established for the production of high purity chromium from solutions containing fluoride or fluosilicate at 38-45 per cent efficiency[39]. The theoretical aspects of deposition from ammonium chrome alum solutions have been studied with reference to cathode current density, potential and efficiency[40]. Ductile chromium has been obtained from a fused salt bath containing potassium chromium fluoride and sodium chloride[41]. There is another report on fused salt electrolysis of chromium chloride-sodium chloride mixture[42]. There are two papers on deposition from fluosilicate solutions containing strontium sulphate[43,44] One of these baths is of the self-adjusting type and is also less sensitive to temperature changes than the conventional bath[43]. Deposits from a chromic acid bath containing strontium sulphate have been recommended for the reforming of automobile and tractor parts[45]. A chromic acid bath with trichloroacetic acid and other additives has also been mentioned[46].

Bright, crack-free plates have been obtained from solutions containing sulphate and fluosilicate ions[47]. For improved wear resistance anodizing has been found to be a suitable step during the chromium plating on aluminium alloys[48]. An evaluation has been made of chromium plates on thorium and uranium for corrosion protection and bonding[24]. Machine parts exposed to tropical climates, sea water and conditions requiring not only corrosion resistance, but hardness and wear resistance as well are cold chromium plated over a nickel base to give a finish which equals cadmium in corrosion resistance and surpassses it in other physical properties. Chromium was plated from an electrolyte containing chromic acid, sodium sulphate and sodium fluoride at an efficiency of 18-20 per cent[49]. A black chromium plating process, which gives hard, wear resistant deposits from a fluosilicate bath, has been described[50]. A chromic acid bath has been suggested for the plating of worm-gears[51]. A similar bath containing colloidal silica has been used for the production of bright, corrosion resistant plates on aluminium and its alloys[52].

Cadmium:

The sulphate and iodide baths with glue[53], and baths of the cyclohexyl ethylenediaminetriacetic acid and sulphamate[54] type have been used recent times. To avoid hydrogen embrittlement the following solutions have been employed: sulphate-glycine, acetate in methyl alcohol and sulphate - triethanolamine[55,56]; complex type with ammonia and amino acids[57]; acetate-triethanolamine-methyl alcohol, and pyridine complexes[58]; iodide-ethylenediamine in dimethylacetamide or dimethylformamide[59]. The pyridine solutions gave semi-bright deposits with good efficiency and throwing power. Cyanide solutions with additions of nickel or cobalt sulphate, sodium dibutyl naphthalene sulphonate and hydroxymethyl cellulose gave bright, adherent and tarnish resistant plates[60]. Other beneficial additions include triethanolamine[61] and polyethylene glycols[62] to the cyanide bath.

Iron and Cobalt:

Plating solutions for iron include various types: sulphate-chloride-citric acid which gave deposits much more wear resistant than those obtainable under ordinary conditions[63]; sulphate-glycine[64]; phenol - sulphonate[65]; fused chloride[66]; sulphamate[67]; and pyrophosphate[68]. Deposits suitable for restoration of worn parts have been obtained from chloride solutions containing additions like glycerol, sugar and dextrin[69]. The chloride bath has been reported to be satisfactory for plating on semiconductors[70], and the fluoborate for micro-wave tubes[71] and for the lining of cylinder walls.[72]

Cobalt has been electrodeposited with the following solutions: sulphate on titanium base[21]; sulphate with organic additions like amino acids[73]; supphamate[74]; and pyrophosphate[68].

Zinc:

Recent work covers plating from solutions of the cyclohexylethlyenediamine triacetic acid[7], thiocyanate[75], ammoniacal[76], pyrophosphate[77] and sulphamate[54] types. The throwing power

of the ammoniacal electrolytes was 30 per cent more than that of an acid bath.

Lead and Indium:

Investigations have been reported on lead plating from nitrate[78], chloride[79,80], pyrophosphate[9,81,82], tartrate[83], acetate[84], fluoborate[85] and sulphamate[86] solutions. To improve the quality of the deposit several addition agents have been used: glucose, glue, gelatin, beta-naphthol, resorcinol, rosin, paracresol and hydroquinone. The fluoborate with various organic addition agents was developed for high speed strip continuous plating. Indium has been deposited from tartrate[73], sulphate[86], chloride[87], EDTA[88] and cyanide[89] baths.

Tin, Bismuth and Antimony:

Fluoride[90], sulphate[91,92] and chloride[92] baths with additions have been employed for high speed tin plating. Others include the fused bath containing beryllium as an additive for plating on aluminium in ultrasonics[93], fluoborate[94] and pyrophosphate[95]. Plating baths attempted for bismuth plating are: phenolsulphonic acid[96], chloride[97] for bismuth-nickel alloy plating on aluminium, perchlorate[98] for plating on semi conductors, and tartrate[99]. Deposition from citrate[100,101] and fluoride[102] baths has been reported for antimony, mirror-bright deposits being obtained from the former.

Titanium, Zirconium and Thorium:

Aqueous solutions attempted for the plating of titanium are of the following types: titanate[103,104], fluoride[104], sulphate[105], solutions containing Ti0++ for plating on semiconducting films of stannic oxide[106], alkaline solutions of fluoride with hydrazine hydrate[107], tartrate[108], chloride in liquid ammonia[109] and chloride[110]. Fused salt baths containing chloride[111-115], bromide[116], and fluoride[117] have also been attempted. Operating data are: plate thickness 4-15 μ, current density as high as 40 amp/dm^2 in aqueous and 160 amp/dm^2 in fused salt solutions, and superimposition of a.c. on d.c. The fluoride bath has been used for the plating of zirconium on uranium[118], and the oxalate for plating thorium on nickel-plated-aluminium or stainless steel[119].

Precious Metals:

The plating of precious metals has gained importance in recent years. Applications include[120,121]: relatively thick deposits in the industry — for electrical contracts; in the decorative field because of their colour and brightness; and in the engineering field. Silver has been elctrodeposited from solutions containing thiocyanate[75,122-124], iodide[124], chloride[125], sulphamoylbenzoic acid[126], and thiosulphate[127] for ceramic and other non-cond ucting bases. Developments in plating from the cyanide bath relate to PRC plating for electronics industry[128], plating on alumiminium[129,130] and bright plating[131,132]. Citrate gold baths have been used for printed circuits[133-135]. Cyanide baths have been used for corrosion, wear and tarnish resistance[136], plating on semiconductors[137], for ball bearings to improve the corrosion resistance[138], plating with solutions containing Ni-EDTA to obtain bright and hard plates[139], plating on silicon[140], bright plating with additives like silver[141], and solutions containing citrate and EDTA for plating on semiconductors[142]. Sulphite solutions containing di-sodium-EDTA have also been mentioned[143].

The baths used for platinum plating are: chloride-disodiumhydrogenphosphate for thick deposits up to 200 μ[144]; dinitrosulphate for bright plating[145,146]; dinitrodiamino complex in sulphuric and phosphoric acids to obtain thick and bright deposits[147]; similar complex in sulphamic acid for the production of low-stress deposits[148]; hexahydroxy platinum[149]; and diamino dinitrate-fluoborate for non-ferrous metals[150]. Recent literature covers the following baths for iridium: cyanide melts for plating on molybdenum or stainless steel, thin coatings affording excellent protection to molybdenum at 1000°C; chromium, nickel and gold strikes are successively applied on the molybdenum base[151]. It is reported that this bath can give plates with thickness up to 3 mils[152]. Chloroiridate solutions[153,154] give plating speeds of 2 μ per hour.

Sulphate baths[155-158] appear satisfactory for the plating of rhodium on silver for protection against attack by hydrogen sulphide, the deposit thickness being of the order of 0.1 μ; and on titanium base for use in electrochemical processes in cathodic protection systems and electrical contacts. The perchlorate bath has also been employed[158,159]. Palladium has been plated from dihydroxyldiamino palladium solutions on metals as well as non-metals[160]; and from ammonium sulphamate-nitrate solutions which avoid the disadvantages of the acid baths and the high temperature required for conventional alkaline baths[161]. Plating solutions for ruthenium are the following: tetrachloride and sulphate[162]; trichloro-

nitrosoruthenate, the suggested applications being as anode or as a base for cladding or plating[164]; nitrosyl sulphamate[164]; sodium-tetra-sulphamatonitrosyl ruthenate[165]; and a cyanide melt[153] suitable for plating up to 2 mils.

Other Metals:

Quite a number of other metals have been referred to in literature, but the information available is rather meagre in many cases. The metals and the plating baths for each are the following: beryllium-fused chloride[166-168]; aluminium-sulphate[169], fused chloride[170] and fluoride[171], hydride in ether solution[172], chloride in formamide[173], bromide in benzene[174] and sodium fluoride-aluminium triethyl[175]; molybdenum-fused halide[42] and pyrophosphate -chloride-borate[176], molybdate in anhydrous glycerol[177]; tungsten-fused halide[42]; uranium-acetate[178], fused chloride[168]; actinides-chloride[179], fluoride[180] and organic baths[181,182]; manganese-chloride[183]; rhenium-perrhenate[184,185]; gallium-aluminate[186,187], chloride[188], and sulphate containing cyanide and carbonate for semi-conductors[189]; magnesium-chloride in anhydrous dimethyl formamide[190]; boron-chloride melts[191]; tantalum-chloride in ethyl alcohol for plating on aluminium foil[192]; selenium-selenous acid, for plates up to 30μ on bright nickel[193].

CONCLUSION

It is seen that the field of single metal deposition has expanded considerably during the period under review. The progress relates in particular to new uses for existing metals, application of coatings of the unusual metals for specialized service, addition agents for bright plating and modification of bath composition to obtain deposits with exceptional properties. It can be hoped that these developments will receive a greater impetus in the years to come.

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