ELECTRODEPOSITION OF CADMIUM AND ITS ALLOYS

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ABSTRACT

The developments in the electrodeposition of cadmium and its alloys since 1965 have been reviewed with special reference to heoreticalt aspects, plating baths, general techniques, properties and applications.

I. INTRODUCTION

Cadmium plating is of importance from the view-point of corrosion resistance as well as a pleasing appearance, and is generally used indoors. The electrical industry makes use of the cadmium plate on steel and other metals because it is easily soldered to and has low contact resistance. For outdoor exposure heavier deposits are extensively applied on steel components. For protection of ferrous metals against corrosion, cadmium is more expensive than zinc, but has many advantages including better performance in the marine atmosphere. The resistance of the cadmium plate to chemicals is, however, generally quite low.

The cyanide bath is commonly used for the deposition of cadmium in view of its good throwing power and ability to give smooth, fine-grained deposits. But hydrogen embrittlement is frequently experienced when plating on high-carbon, high-alloy or stainless steels. In view of this and the desire to develop non-poisonous solutions, there has been a search for other types of baths. The fluoborate and Sulphamate baths have been developed in this direction. The former possesses the advantages of high current efficiency and plating speed, stability, very little hydrogen embrittlement and very broad application in barrel plating. Its chief disadvantage is poor throwing power. The sulphamate bath has the poorest throwing power, but gives deposits which are less porous at a high cathode efficiency. The literature up to 1965 has been well covered in books and journals [1-7].

In the field of alloy deposition there are interesting possibilities in the codeposition of cadmium with silver, zinc, nickel, tin and indium. However, cadmium alloys have not established themselves in commercial plating as much as some other alloys. It will be worthwhile to go in for the deposition of cadmium with a cheaper metal and obtain an alloy which has the essential properties of the former. The developments up to 1965 have been described in earlier literature 3,8-14 This paper outlines the progress in the deposition of cadmium and its alloys during the period 1965-1967.

II. CADMIUM

(A) Theoretical Studies

The effect of the hydrogen ion on the cathode polarization during the deposition of cadmium from sulphate solutions has been studied. Increasing the concentration of sulphuric acid from 0.1 to 3N shifted the equilibrium potential to more negative values, and resulted in a plateau corresponding to the limiting current for the discharge of the cadmium ion. The latter decreased with increase in the acid concentration.[15] The high current efficiency even at low current densities of the order of 0.2-—0.5 amp/dm^2 in solutions with a high sulphuric acid and low cadmium concentration has been found to be due to the excessive polarization for the discharge of the hydrogen ion[16]. The oscillographic method has been used to obtain the potential-time curves during deposition from sulphate solutions also containing zinc[17]. The effect of temperature, rate of electrode rotation and the use of ultrasound on the cathode polarization during deposition from cyanide solutions indicates that at high negative potentials polarization is essentially of the concentration polarization type[18]. The thickness of the diffusion layer is calculated to be 0.02 cm, and the diffusion coefficient in cyanide, with cyanide and alkali supporting electrolyte 3.15 $\times$ 10-^{6} cm^2/sec.

Cathodic potentiostatic polarization curves

(C) Plating Baths

1. *Complex Type*

Additions of the cupric and halogen ions are reported to shift the potential in a negative direction during deposition from ethylenediamine electrolytes[36]. These solutions have also been used for brush plating[37]. Another paper reports the operating conditions and properties of deposits obtained from solutions containing ethylenediamine as well as ammonium chloride[38]. Detailed studies have been made on the deposition of cadmium from ammonium sulphate complex as well as fluoride complexes. The cathode efficiency is quite high, 90-100 per cent. The relationship between the limiting current density and concentration of the cadmium complex points to a direct discharge of the complex and to diffusion as the rate-determining step. Replacing the cadmium oxide by the sulphate in the plating solution considerably increases the limiting current density but causes a deterioration in the quality of the coating. Polarization curves show an inflection due to the reduction of the cadmium ion at lower, and of complex cadmium ions together with cadmium ions at higher potentials. Addition agents like thiourea, dextrin, glue, orthocresol, saccharin, coumarin and glycine had a beneficial effect on the deposits from the sulphate bath. Their effect on the fluoride bath was less probably due to a preferential adsorption of the fluoride ion which reduces the adsorption of the organic compounds at the cathode. Increasing the temperature or agitation of the solution was not helpful. The effect of pH on the polarization has also been studied, and the best deposits obtained in the 7-9 range of pH[39]. There are two more papers covering the sulphate complex[40,41].

High quality coatings have been obtained from solutions containing aminoacetic acid and sodium chloride together with additions of gelatin and thiourea. The corrosion resistance was high in the spray of a 3 per cent sodium chloride solution. The cathode efficiency was close to 100 per cent, and the throwing power of the solution about the same as that of the cyanide[42,43]. Bright deposits with a current efficiency of 70-98 per cent have been obtained up to 10 amp/dm^2 from alkaline EDTA electrolytes[44]. The effect of several additions forming complexes have been tried: glycine, Trilon B, ammonium sulphate, aluminium sulphate, boric acid, ammonium fluoride, amine, urea and dextrin, and the first three substances gave the best deposits with satisfactory throwing power due to an increase in the polarization[45]. There are two papers[46,47] covering the production of quality deposits from the pyrophosphate complex bath at 25-60°C and the limiting current density of 5 amp/dm^2. Complex solutions containing hexamethylenetetramine[48] have been reported to give satisfactory deposits, with the beneficial effect of addition agents like glue, dextrin and gelatin. The chloride ion addition eliminated passivation of the cadmium anodes, the limiting anode current density being 4 amp/dm^2. Satisfactory deposits have been obtained on copper from tetramethylurea solutions[49]. Quality plates at high electrode efficiencies have also been obtained from mercapto-complex baths with good throwing power : 2-mercaptoethanol, mercaptoacetic acid, mercaptoethylamine and 1-thioglycerol[50]. The development of an ethanolamine complex plating bath has been cited[51]. Solutions containing cadmium sulphate and ammonium or potassium thiocyanate[52] together with aniline hydrochloride and glue have also been used for cadmium deposition at a pH of 3-5 and up to 2 amp/dm^2.

2. *Others*

The sulphate bath containing cresol sulphonic acid and addition of sodium chloride has been employed for the deposition of electrochemically active deposit—dull grey and coarse, with a nickel-containing working electrode[53]. The electrodeposition of cadmium coatings with improved mechanical properties from electrolytes containing suspensions of non-conductive solid particles was studied. Deposits with 0.5—3.0 per cent corundum inclusions have higher micro-hardness and abrasion resistance[54]. The sulphamate bath[55] has been studied for the plating of cadmium on steel, the operating conditions being: cadmium concentration 0.6—3.7M, pH 0.5—4, 20—40°C and 4-90 amp/dm^2. Various additions were tried and very bright deposits obtained with 2-3 g/l polyvinyl alcohol in 2-2.2M cadmium at a pH of 2.5 and 30 amp/dm^2. Another paper covers studies on the morphology and structure of deposits from this bath on single crystal cathodes. Details of the orientation under different conditions, particularly current density and thickness of the deposit, have been given. Although the plates were lustrous the hardness was less than that of the base[56].

The comparative characteristics of various plating solutions[57] have been studied; they contain cadmium sulphate or oxide and ammonium sulphate, sodium sulphate, naphthalene

disulphonic acid and gelatin, ammonium chloride and mono-ethanolamine with glue, ammonium sulphate with thiourea and glue, ammonium sulphate and urotropine with bromide and glue, sodium sulphate and cyanide. Most of them gave silvers-smooth plates at an efficiency of 90-100 per cent, the throwing power being quite good, 20-67.5 per cent. They adhered well to the base and were pore-free when thicker than 7μ. Another paper covers laboratory and pilot plant studies from sulphate, oxalate, fluoborate and pyrophosphate electrolytes. The advantages claimed are: lack of toxicity, low cost, simplicity in composition, lower susceptibility to harmful impurities, higher current efficiencies and higher stability [58].

Three papers deal with the fluoborate bath. The first one is meant for decorative and engineering purposes. Substances like gelatin, licorice and glue have been used to obtain bright plates [59]. ^{109}Cd has been plated on to copper wire to prepare soft X-ray sources for thickness gauges [60]. Mounting parts for equipment destined for exposures in tropical climates have been plated from this bath. The film thickness of 12 μ requires 30 minutes at a current density of about 1 amp/dm^2, and the plate has a fine-grained structure [61]. To avoid hydrogen absorption and obtain a deposit with good adhesion, a molten bath[62], of cadmium and sodium chlorides has been operated at 420-450°C and 10 amp/dm^2. From a comparative evaluation of plating from non-cyanide solutions, it is found that good results are obtained from solutions of complex ammonium salts. The prospects for the further development of electrolytes based on amino compounds are pointed out [63].

(D) Bright Cadmium

The brightness and throwing power of the cyanide bath for cadmium plating have been improved by the addition of the reaction product of hexamenthylenetetramine and epichlorohydrin or alpha-chloroglycerol in approximate equimolar amounts and 1 to 2 parts water. The reaction products are soluble in water and stable in alkaline solution but tend to decompose in the presence of oxidising acids [64]. In another paper alpha-napthylamine sulphate and a wetting agent are added to a cyanide solution to obtain a bright plate at a current density of 1.3—3.5 amp/dm^2 with periodic reverse current [65]. A combination of betaine together with the polymeric proteins, albuminoids, or synthetic compounds are stated to be effective brighteners in cyanide plating [66]. Another additive from the view-point of brightening is a solution containing the product of oxidation of a water-soluble poly (vinylate) with hydrogen peroxide, alkali metal permanganates, or alkali metal dichromates and cadmium in the form of a complex alkali metal cyanate [67].

The influence of different types of cobalt (III)—ammine complexes in acid and alkaline cadmium plating baths on the formation of bright cadmium coatings, using the Hull cell has been recently studied. Cyanide electrolytes gave better results than the sulphate, the added complexes being beneficial up to a concentration of 0.1 g/l. Many additives gave mirror-bright deposits. Details concerning the type of the complex and the ligand, as well as their effect on the quality of the coatings have been described in detail [68]. The barrel plating of radioactive silver (^{110}Ag) by immersion deposition on copper shear pins and subsequent cadmium electrodeposition for corrosion protection and to prevent rub-off of the radioactive silver during handling, has been described. The appearance of the plated pins was excellent, being covered with a bright cadmium deposit; in no case was copper visible [69,70]. Another brightener for the acid bath is a 0.03—1 weight per cent of a polyamide [71]. Sulphur-containing phosphate derivatives, 0.001—20 g/l, have been added as brightening agents to cadmium plating baths [72]. Surface-active substances are found to lower the differential capacity of the double layer at the mercury-solution interface in sodium sulphate and cyanide solutions. Polarization curves for deposition of cadmium from simple sulphate solutions and from sulphate solutions containing ammonia or sodium cyanide showed that additives retarded the deposition process, thus producing finer crystals and better coatings from the solutions in which the cadmium was complexed. This is because deposition from the complex occurs at a potential corresponding to maximum adsorption of the additive [73].

(E) Properties

In relation to the hydrogen embrittlement testing of high-strength steels, caused by electroplating, a study was made of the thickness of cadmium coatings deposited in V-notches of various angle cut in 3 per cent chromium-molybdenum-vanadium steel, marquenched from 940°C and tempered at 310°C to give tensile strengths of approximately 120 tons/in^2; plating was from a cyanide bath to a thickness of 10 μ on the open surface. In angles varying from 45 to 90°, the cadmium thickness at the notch root increased with

notch angle; in the 90° specimen this value was about half that of the free surface. Recommendations are made on preferred coating procedures for notched specimens[74]. For a better understanding of the relationship between deposit thickness and the principal variables related to the part design, studies have been made with specimens plated from a cyanide bath with respect to the following factors: diameter and depth of the cavity and distance of the anode from the cavity opening. It was found that the depth of the hole as well as the anode distance have a significant influence on the deposit thickness, but not the diameter of the hole. Using regression analysis techniques a relationship has been found between the deposit thickness and hole depth for a given electrode distance[75].

A relationship between plating thickness and shape of the product to be plated, as well as the durability and corrosion resistance have been reviewed[76, 77]. Electrodeposition in a bell, in a drum, and in a combination of both has been discussed[78]. It has been shown that the distribution of the most frequently encountered heights at a local point of the metal deposit interface is governed by the Gaussian integral curve of normal distribution. Cadmium was deposited from a solution containing the metal oxide and ammonium sulphate together with additions of dextrin and thiourea [79, 80]. The throwing power of the cadmium sulphamate bath, studied with the Hull symmetrical cell, has been reported to be poor[81].

The internal stresses of cadmium coatings obtained from the ammonium sulphate complex bath have been investigated by measuring the bending of the samples of the plated cathode. The expansion of the deposit is inversely proportional to the average size of the crystals. The hydrogen enrichment during deposition and subsequent removal of hydrogen has no substantial effect on the expansion and the shrinking following. A thorough purification of the deposition bath reduces the expansion. It is assumed that impurities may have a decisive effect on shrinking. The shrinking of the deposit after electrodeposition is attributed to the structural changes, recrystallisation, and polygonisation, of the coating[82]. The roughness of deposits from the sulphate bath has been found to be inversely proportional to the current density initially, but on prolonged passage of current it was directly proportional. Deposits from the ammonium sulphate complex and fluoride electrolytes were more rough than those from the sulphate bath for a given thickness[83].. The hardness and frictional properties of cadmium used for the plating of jet engine parts have been discussed[84]. The addition to the plating bath of the sodium p-toluyl chloroamidosulphonate is reported to give glossy coatings without cooling the electrolyte[85].

Addition of inorganic cations like aluminium, sodium, manganese, zinc and nickel in small concentrations to a sulphate bath results in the considerable reduction in the grain size together with the change in the grain shape of the coating. These effects are attributed to a decrease in the cation concentration in the vicinity of the cathode layer as a result of expulsion of foreign cations from it and to adsorption of the chief compounds of the added cations[86]. An alkaline storage battery electrode has been prepared by plating from a chloride solution[87]. Another patent describes the preparation of negative electrodes for use in the alkaline galvanic cell, by plating a conductive metal matrix with the second metal. A cadmium nitrate solution is used together with a cadmium electrode forming a complex cadmium oxide-cadmium nitrate, the latter being easily washed away. The operating conditions are: pH 1.4—2.3 with nitric acid, 20—30°C and 0.45—90 amp/dm^2 cathode current density. The opening size of the square holes ranged from (0.015)^2—(0.045)^2 sq. inch. This method can also be employed for plating from chloride or acetate solutions[88]. A plating plant with programmed control has been described[89].

(F) Miscellaneous

A method is reported for improving the brilliancy and corrosion resistance of conventionally chromated articles of electroplated cadmium. The chromating is done from a solution containing a titanium salt at a pH below 1.5 for 5 Seconds, washed with water and dried in air for 5 seconds at 20—30°C. It is then suspended in air for 5—6 hours at 70°C. A plated article subjected to this treatment withstood the 50 per cent sodium chloride spray for 288-312 hours, as against 96 hours for the usual chromated article[90]. The phosphating of cadmium-plated steel has been studied by changes in the weight, potential, pH near the cathode layer and quality of the film[91]. Quantitative test methods have been used to assess organic surface coatings for emission of vapours likely to attack cadmium plate, for the protection of cadmium against attack by aliphatic acids, and for long term retention of adhesion on exterior exposure. None of the coatings tested was free from a tendency to attack cadmium plate under the conditions of test. Chlorinated rubber lacquers

trolled radiometrically with ^{115}Cd. The effect of thiourea labelled with ^{35}S, in addition to other surfactants on the deposition was studied[101].

(B) Cadmium-Copper

A comparison has been made of the structures, as examined by the X-ray powder technique, of copper-cadmium alloys in the range 14-99 per cent cadmium, prepared by melting and casting and by electrodeposition from the cyanide bath at a constant cathode potential. The existence of metastable alloys in the as-deposited state, and their transformation on annealing to the equilibrium phases found in the melt-formed alloy are discussed—from the points of view of the cathode potential and of the disappearance of the preliminary codeposited hydrogen, thereby causing rearrangement of the atoms discharged from the disordered state to form stable or metastable phases. The cathode potential during deposition decreases from 2.27 to 1.15 volts, and the potential range for the different phases from alpha to eta has been determined[102].

Electrodeposition of these alloys from cyanide solutions was studied at frequencies of 18.5 and 38 kc. and at acoustic intensities equal to or less than 0.5w /cm². Marked changes occurred in the composition of the deposited alloys. Some ultrasonic deposits. were brighter, harder, more adherent, or of finer grain size than non-irradiated deposits. The irradiated deposits were also smoother and less porous and they afforded better corrosion protection for the substrate metal in sodium chloride solution. The copper content was lowered by ultrasonics. Cathode efficiency was increased by as much as 36 per cent, and anode corrosion was doubled in some cases. Cell voltages were lowered by 50 per cent in many tests. The acoustical system consisted of 2.5—3 l. polythylene electrolytic cell and a magnetostriction or barium titanate transducer assembly, both immersed in a constant temperature water bath, and an ultrasonic generator [103] having an average power output of 250 w. at 18.5 kc.

Detailed investigations have been made on the phase structure of alloys deposited from citric acid, ammonia and cyanide complexes. From the first bath a supersaturated solution of cadmium in copper was obtained. The cadmium content in the alloy deposited from ammonia electrolyte coincided with its solid solution concentration, and it is concluded that the deposits are single-phase solid solutions. The study of the phase structure of the deposits from the cyanide bath showed either a strongly oversaturated solid solution of copper base, or a phase with strongly distorted crystal lattice. Citric acid produced a phase of metastable compound of liquid-like structure, whereas in ammonia a one phase solid solution up to relatively high concentrations of cadmium in the alloy was obtained. The reduction of ions of copper and cadmium from cyanide solutions takes place at relatively high negative potentials. The alloys with 15-80 atomic per cent cadmium have a liquid-like structure[104]. Work has also been carred out from solutions containing copper, cadmium, sodium and ammonium sulphates together with ammonia and addition of dextrin at a pH of 8.3—8.6 and 17-25°C with alloy anodes. The current efficiency was 95-96 per cent and the rate of deposition 0.5—0.8 μ/min. The throwing power of the solution was 41 per cent, and the deposit silver-bright and fine-grained[105] with a microhardness of 330-60 kg/mm².

The effect of surface-active substances on the phase structure of alloys plated from sulphate solutions has been studied. X-ray analysis indicated the formation of an oversaturated solid solution of cadmium in copper, an alloy with liquid-like structure, and a compound $CuCd_3$, with an increase in the cadmium content. Organic substances had little effect on the structure. The codeposition of copper was strongly inhibited with increase in the cadmium content of the alloy obtained from electrolytes containing sulphuric acid without and with surface-active substances. This inhibition is attributed to a change in the structure of the electrical double layer and increase in the adsorption of the additives[106]. Two more papers discuss the structure of these alloys. The formation of supersaturated solid solutions on a copper base aided formation of compact, smooth deposits at potentials at which copper is deposited under limiting diffusion current conditions. Cadmium in the copper lattice hindered copper deposition. Inhibition of copper deposition is due to a change in the potential difference at the metal - solution interface as a result of a shift in the zero charge point of the alloy with increase in the cadmium content[107, 108].

(C) Cadmium-Nickel

Electrodeposited alloys of nickel with cadmium are promising in the decorative and protective finishing of metals, the possible applications being for bright plating, bearings, engine cylinders, jet engine parts, electrical contacts and in batteries. Attempts have been made to deposit a cadmium-nickel alloy from

additives like gelatin, thymol, beta-naphthol and diphenylamine[119].

IV. CONCLUSION

It is seen from the above discussion that the recent trends in cadmium plating research relate to investigations of a theoretical and applied character. There is growing interest in polarization studies as well as effect of addition agents. The prevention of hydrogen embrittlement and the production of bright cadmium has attracted considerable attention. With a view to evolve a substitute for the cyanide bath, complex salt baths as well as simple salt baths with additions have been tried, and many of them appear to be promising. Several papers are devoted to the properties of the cadmium plate, since this has a direct bearing on the commercial application. In the field of alloy deposition considerable work has been carried out, during the period under review, on alloys of cadmium with zinc and copper, followed by nickel and cobalt. Other alloy systems have received little attention. Several baths appear to be suitable, but the development will depend upon the possible application. The structure of alloy deposits and the mechanism of codeposition have been considered in detail for some systems. There is, however, need for further work before cadmium alloys can find a reasonable place in industrial plating.

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