Electrodeposition of Cobalt Alloys

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ABSTRACT

The electrodeposition of cobalt alloys has been reviewed with special reference to types of alloys, plating baths and industrial applications.

INTRODUCTION

The electrodeposition of alloys of cobalt with various metals has come to prominence in recent years, although cobalt plating itself is not commonly practised. These alloys find application in the decorative and protective finishing of metals, since they are hard, bright and corrosion resistant. Further, they are of importance to the electrical industry, and particularly in the field of electronics. Although developmental work has not attained a fruitful stage in the case of many alloys, an attempt will be made in this paper to present in broad outline the recent progress in the field of cobalt alloy deposition. The investigations carried out in this laboratory have also been reported.

COBALT-NICKEL ALLOYS

Cobalt has been codeposited with nickel from various types of solutions: sulphate[1], chloride[1,2-4], sulphate-chloride[5], triethanolamine[6], sulphamate[7-9] and pyrophosphate[10]. Alloys with a low cobalt content up to about 5 per cent are used in bright plating; high cobalt depositis with 25–45 per cent find application in protective finishing. Plates with as low as 1 per cent cobalt have unusual softness and ductility that permit relatively easy buffing. A deposit with 40 per cent cobalt has been used as a bright, white undercoat for chromium and rhodium plate. These alloys have been stated to have some advantages for finishing of magnesium alloys.

Recent applications are for tape recording and as transducers. In the former case this alloy plate is said to be better in view of a higher remanence and lower coercivity. For magnetic properties, deposits containing 60-80 per cent cobalt are generally used[1-4,7,8]. A minute quantity of potassium thiocyanate in the chloride solution has been reported to improve the quality of the deposit for magnetic uses[8]. Sulphate or chloride electrolytes without any addition agent have been found to be the best from the view-point of coercive force and residual induction of the deposit. Superimposition of the A.C. raises the coercive force and reduces the remanence.[4] The coercivity is increased with the absence of boric acid in the bath, and changes in magnetic properties do not appear to be related to changes in the deposit composition alone.

ALLOYS OF COBALT WITH IRON AND ZINC

Cobalt-Iron : The baths used for cobalt-iron alloy plating are : sulphate[11,12], chloride[11,13], sulphate-chloride[14], sulphamate[15] and pyrophosphate[16,17]. Rotinyan and Molotkova[18,19] have studied the cathode polarization during the simultaneous discharge of cobalt, iron and hydrogen ions from sulphate solutions. The deposits from the sulphate bath adhere tenaciously to stainless steel[11]. An alloy containing about 50 per cent iron has been stated to be suitable for bonding aluminium to steel[20]. Investigations have also been carried out recently with a view to extend the use of alloy plates from chloride solutions in the restoration of worn out parts[21].

Cobalt-Zinc : Codeposition of cobalt with zinc has been studied from sulphate solutions[22,3], and the radioactive tracer method has also been used[24,26]. Recently the pyrophosphate bath has been found to be suitable for the plating of quality deposits containing 0-99 per cent zinc[27]. Further research in this direction might establish the plating of the alloy on an industrial basis.

ALLOYS OF COBALT WITH TUNGSTEN AND MOLYBDENUM

Cobalt-Tungsten : Codeposition of cobalt with tungsten is of industrial importance in view of the special properties of the alloy plates — brightness, hardness and resistance to tarnish

and corrosion[5,28]. The electrodeposition of these alloys has been carried out from citrate[5,28,29], tartrate[5,28], sulphate[5,28,30,31], sulphate-chloride[32] and pyrophosphate baths[33]. The microhardness of the alloys was found to be doubled by heat treatment. With increasing tungsten in the coating internal stress as well as current efficiency were reduced. The alloy proved highly stable in atmospheres of sulphur dioxide and nitrogen peroxide. The best protection against 3 per cent sodium chloride was in a deposit containing 35 per cent tungsten[30]. Roy and coworkers[29] have pointed out that the plates are suitable for application to gun barrels, tools, dies, piston rings, bearings and other materials. In a study on the magnetic characteristics of the deposits it has been found that the presence of sodium hypophosphite and ammonia in the electrolyte increases the coercivity of the alloy[32]. The corrosion resistance of alloy deposits of tungsten with cobalt in acids like hydrochloric and nitric was better than those of alloys of nickel and comparable to alloys with iron[34]. These alloys are also promising substitutes for the chromium plate.

Cobalt-Molybdenum: As in the case of tungsten, molybdenum has also been deposited from aqueous solutions in alloy form with cobalt, nickel, iron and other metals, and some of these plates are bright, white, hard and fairly adherent[5]. The alloys have been deposited from citrate solutions[35-37], and recently the pyrophosphate bath has been shown to be suitable[38,39]. Ernst and Holt[40] have measured the cathode potentials during codeposition and discussed the mechanism of the molybdenum plating process. The alloys are metallic and either bright or light grey in appearance, with a large number of cracks in the bright deposits[36]. The addition of hydrazine sulphate to the plating bath prevents the anodic oxidation of cobaltous ion and increases the cathode efficiency as well as the molybdenum content of the deposit. The latter tarnishes readily without a protective coating[38].

Although the deposition of alloys of cobalt with tungsten and molybdenum is rather expensive, it might find justification in specialized applications wherein the unusual properties of the electroplates are badly needed.

OTHER BINARY ALLOYS

Cobalt-Chromium: Recent reviews [41,42] on the electrodeposition of cobalt-chromium alloys indicate that there has been little development in this field. Humphries[43] has taken a patent on the electrodeposition of the alloy for razor blade edges, and Candussi[44] claimed codeposition on steel and aluminium base. Baths containing trivalent chromium has been used by many workers[45-47], and appear to be very significant in view of the higher efficiency and deposition rate. The solutions are of the sulphate type, with additions like ammonium sulphate or sulphamate and fluoborate. Bright deposits have been obtained recently by the addtion to an acid bath of organic compounds belonging to different types: amides or imides, sulphonic and carboxylic acids, alcohols and esters, or heterocyclic bases and alkyl halides[48]. These alloys are also of interest for high temperature protection of materials. It is expected that further developmental work will lead to plating processes of industrial interest.

Cobalt-Manganese : Cobalt has been codeposited with manganese from sulphate solutions[49-52]. The deposits were bright, adherent and corrosion resistant; in the latter aspect the plates were more resistant than mild steel to corrosion by tap water.

Cobalt-Tin : There is little information on electrodeposited tin-cobalt alloys. A plating process for the production of adherent but brittle alloy deposits with the chromium colour has been described[53]. A chloride-fluoride bath similar to that for tin-nickel deposition has been mentioned for tin-cobalt alloys also[54,55]. It has been recently reported that the pyrophosphate bath is satisfactory for the production of quality deposits over a wide composition range[56].

Cobalt-Copper : Fink and Hutton[57] could not obtain a 50 per cent cobalt alloy electrolytically. These alloys have been reported in some papers[58-60], but details are not available. Detailed studies in this laboratory have shown that it is possible to obtain satisfactory deposits containing 1-94 per cent cobalt from the pyrophosphate bath[61].

Miscellaneous Alloys : The codeposition of cobalt with other metals has been reported, but the information available is rather meagre. The alloying metal and the plating baths for each system are: (*a*) silver-thiosulphate or bisulphate[62], and cyanide[63], (*b*) gold-cyanide[64], (*c*) titanium-[65,66] fluoborate and (*d*) rhenium-citrate[67,68].

TERNARY ALLOYS

Electrodeposition of ternary alloys has not been studied to the same extent as binary alloys. It is no doubt an attractive field. Alloys of cobalt with nickel and iron have been deposited from sulphate-chloride[69,70], sulphate[71,72], alkaline[73] and pyrophosphate[17] solutions. They are magnetic and also resistant to humid and gaseous media. The

pyrophosphate bath appears to be suitable for the plating of ternary alloys of cobalt and zinc with iron[17] or tin[27] or nickel[27] or copper[61]; and cobalt and nickel with tin[60] or copper[61]. Mention may be made of cobalt-tin-copper alloys from the cyanide bath[74], and of cobalt-nickel-palladium alloys from the sulphate baths[75].

In systems involving tungsten, pyrophosphate solutions have been shown to be suitable for the deposition of alloys of cobalt and tungsten with iron[17,33] or copper[33,61] or zinc[27,33] or tin[33] or nickel[76]. The last alloy has also been plated from sulphate-chloride solutions[77]. Alloys of cobalt-tungsten-molybdenum have been obtained from citrate[78] and amine[79] type of baths.

GENERAL CHARACTERISTICS

The relationship between the ratio of cobalt to alloying metal in the plating solution to that in the deposit will depend upon the alloying metal as well as the type of bath. In the case of zinc, the metal ratio in the solution is very much greater than that in the deposit: It is difficult to obtain binary alloys of cobalt with a high content of tungsten, molybdenum, manganese or titanium. The cathode efficiency is also rather low during the deposition of these alloys. In general, addition agents appear to have little effect on the nature or the deposit or the bath performance. There is a tendency for constancy of composition at higher current densities in most systems. In the case of cobalt-zinc, sudden changes in deposit composition as well as cathode potential have been observed corresponding to changes in the phase of the deposited alloy.

CONCLUSION

It has been outlined above that various alloys of cobalt can be electrodeposited from different plating solutions. Although most of them have not been established for commercial usage, they are expected to enter the field of metal finishing in the near future. The deposition of binary and ternary alloys also bring out many points of theoretical significance. This is specially the case with metals like tungsten or molybdenum which require a catalyst metal for electrodeposition from aqueous solutions. The development of these alloys will, of course, necessitate further research work not only on the electrochemical aspects including anode behaviour, but also on the structure and properties of deposits. It can be concluded that the plating of cobalt alloys, binary or ternary, and if possible quaternary, appears to be a promising field.

REFERENCES

1. V. M. Zhogina and B. Ya. Kaznachei, Trudy Chetvertogo Soveshchaniya po Elektrokhimii, Moscow, 506 (1956); Chem. Abs., **54,** 8357 (1960).
2. B. Ya. Kaznachei and V. M. Zhogina, Trudy Vsesoyuz Nauch-Issledovatel. Inst. Zvukozapisei, No. 1, 91 (1957); Chem. Abs., **54,** 6359 (1960).
3. H. C. Scheer and E. R. York, U.S. Pat., 2,834,725 (1958).
4. V. Zentner, Tech. Proc. American Electroplaters' Soc., **47,** 166 (1960).
5. A. G. Gray (Editor): 'Modern Electroplating', John Wiley and Sons, New York (1953).
6. C. J. Brockman and J. P. Nowlen, Trans. Electrochem. Soc., **69,** 553 (1936).
7. R. C. Barrett, Tech. Proc. American Electroplaters' Soc. **47,** 173 (1960).
8. I. Tsu, Plating, **48,** 379, 1207 (1961).
9. S. Venkatachalam and T. L. Rama Char, Electroplating and Metal Finishing, **15,** 233, 270 (1962).
10. (Miss) Vasanta Sree and T. L. Rama Char J. Electrochem. Soc., **108,** 64 (1961).
11. W. M. Fassel Jr. and J. P. Baur, Astia Document 157789 (1957); Cobalt No. 2, 56 (1959).
12. K. Aotani, Nippon Kinzoku Gakki-Shi B14, No. 5, 52 (1950); Chem. Abs, **47,** 7916 (1953).
13. F. De Marinis, U. S. Pat., 2,507,400 (1950)
14. A. L. Rotinyan and E. N. Molotkova, Zhur. Priklad. Khim., **32,** 2502 (1959); Chem. Abs., **54,** 7371 (1960).
15. S. S. Misra and T. L. Rama Char, Chemistry and Industry, 1908 (1961).
16. (Miss) Vasanta Sree and T. L. Rama Char, J. Sci and Ind Research, **19B,** 223 (1960).
17. D. V. Subrahmanyam and T. L. Rama Char, Chemistry and Industry, 930 (1962).
18. A. L. Rotinyan and E. N. Molotkova, Zhur. Fiz. Khim., **35,** 158 (1961); Chem. Abs., **55,** 10145 (1961).
19. A. L. Rotinyan and E. N. Molotkova, ibid., **34,** 2336 (1960); Chem. Abs., **55,** 11137 (1961).
20. R. A. Schaefer, J. F. Cerness and Wm. H. Morrison, U. S. Pat., 2, 687, 565 (1954).
21. M. M. Lekhikoinen, Trudy Tadzhik, Sel' skokhoz. Inst., **2,** 69 (1958); Chem. Abs., **55,** 5190 (1961).

22. S. Glasstone, J. Chem. Soc., 641 (1927).
23. G. N. Znamenskii, A. F. Mazanko and V. V. Stender, Zhur. Priklad. Khim., **34,** 1305 (1961); Chem. Abs., **55,** 25545 (1961).
24. Z. A. Sheka and K. F. Karlysheva, Doklady Akad. Nauk S. S. S. R., **108,** 126 (1958); Chem. Abs., **51,** 3328 (1957).
25. Z. A. Sheka, Ukrain. Khim. Zhur., **22,** 394 (1956); Chem. Abs., **51,** 108 (1957).
26. S. M. Kochergin and G. R. Pobedimskii, Zhur. Priklad. Khim., **31,** 1432 (1958); Chem. Abs., **53,** 915 (1959).
27. D. V. Subrahmanyam and T. L. Rama Char, Chemistry and Industry, under publication.
28. F. W. Salt, Murex Review, **1,** No. 5, 77 (1949).
29. D. L. Roy et. al., Symposium on Electrodeposition and Metal Finishing, 1957, India Section, The Electrochemical Society 42 (1960).
30. N. P. Fedot' ev **et. al.,** Zhur Priklad Khim., **32,** No. 10, 2235 (1959); Chem. Abs., **54,** 7371 (1960).
31. N. T. Kudryavtsev and N. M. Alpatova, Tr. Mosk. Khim. Tekhnol. Inst., No. 32, 293 (1961); Chem. Abs., **57,** 4459 (1962).
32. B. Ya. Kaznachei and V. M. Zhogina, Trudy Vsesoyuz. Nauch.–Issledovatel. Inst. Zvukozapisei, No. **6,** 119 (1959); Chem. Abs., **56,** 1283 (1962).
33. K. I. Vasu and T. L. Rama Char, Plating, **49,** 60 (1962).
34. T. Kudo and K. Mizuno, J. Metal Finishing Soc., Japan, **13,** 4, 162 (1962).
35. H. J. Seim and M. L. Holt, J. Electrochem. Soc., **96,** 205 (1949).
36. D. W. Ernst, R. F. Amile and M. L. Holt, ibid., **102,** 461 (1955).
37. T. B. Frantsevich-Zabludovskaya, Ukrain. Khim. Zhur., **25,** 463 (1959); Chem. Abs. **54,** 8360 (1960).
38. A. Krohn and T. M. Brown, J. Electrochem. Soc., **108,** 60 (1962).
39. P. C. Rydel and S. C. Barnes, Paper presented at the Boston Meeting, Electrochemical Society, Sept. (1962).
40. D. W. Ernst and M. L. Holt, J. Electrochem. Soc., **105,** 686 (1958).
41. C. Levy, Metal Finishing, **57,** No. 8, 59 (1959).
42. L. F. Spencer, ibid., **60,** No. 2, 48 (1962).
43. C. H. Humphries, Brit. Pat., 343, 336 (1930).
44. M. Candussi, Ital. Pat., 469, 634 (1952).
45. T. Yoshida and R. Yoshida, J. Chem. Soc., Japan, Ind. Chem. Sect., 58, 89 (1955).
46. W. H. Safranek, U. S. Pat., 2,822, 326 (1958).
47. G. R. Schaer, U. S. Pat., 2,927, 066 (1960).
48. Centre national de la recherche scientifique, Fr. Pat., 1,229, 625 (1960).
49. R. I. Agladze and M. Ya. Gdzeshvili, Bull. Acad. Sci. Georgian S. S. S. R., **5,** 975 (1944); Chem. Abs., **4** , 3378 (1947).
50. D. N. Gritsan, E. I. Vail and V. P. Moskovets, Uchenye Zapiski Khar' kov Univ., **50,** Trudy Nauch-Issledovatel. Inst. i Khim. Fakulteta No. 11, 273 (1954); Chem. Abs., **51,** 1732 (1957).
51. I. V. Yanitskii, B. B. Stulpinas and B. Girchene, Lietuvos TSR Mokshi Akad. Darbai Ser., B. No. 3, 69 (1958); Chem. Abs., **54,** 12828 (1960).
52. B. Stul' pinas and B. Girchiene, Pirmoji Respub. Chem. Konf., Lietuvos, TSR Moksu Akad., Chem. ir Chem. Technol. Inst. Vilnyus, 41 (1958); Chem. Abs., **55,** 5191 (1961).
53. Plating Notes, **3,** 15 (1951).
54. F. A. Lowenheim and R. T. Gore, Iron Age, **179,** No. 17, 112 (1957).
55. J. W. Cuthbertson, Metallurgia Ital., **46,** 85 (1954); Chem. Abs., **48,** 11959 (1954).
56. (Miss) Vasanta Sree and T. L. Rama Char, Metalloberfläche, **15,** 301 (1961).
57. C. G. Fink and J. L. Hutton, Trans. Electrochem. Soc., **85,** 119 (1944).
58. G. Bruni and M. Amadori, atti. accad. sci. lett. ed. arti, Padova **30,** 349 fol (1913); Chem. Abs., **9,** 1432 (1915).
59. W. R. Meyer and A. Phillips, Trans. Electrochem. Soc., **73,** 69 (1938).
60. J. Fischer, Metalloberfläche, **1,** 229, 252 (1947).
61. D.V. Subrahmanyam and T. L. Rama Char, Metal Finishing, under publication.
62. P. Marino, Brit. Pat., 102, 828 (1916).
63. Q. Marino, Brit. Pat., 173, 268 (1920).
64. F. Volk, U.S. Pat., 2,812,299 (1957).
65. M. Candussi, Ital Pat., 469, 364 (1952).
66. S. M. Kochergin and G. R. Pobedimskii, Zhur. Priklad. Khim., **33,** 238 (1960); Chem. Abs., **54,** 9547 (1960).

67. L. E. Netherton and M. L. Holt, J. Electrochem. Soc., **99**, 44 (1952).
68. Z. M. Sominskaya *et. al.*, Renii, Tr. Vses. Soveshch. po Probl. Reniya, Akad Nauk S.S.S.R. Inst. Met., 209 (1958); Chem. Abs., **57**, 3186 (1962).
69. R. M. Burns, U.S. Pat., 1,9_0,964 (1933).
70. A. I. Savarets, U.S.S.R. Pat., 147,075 (1962).
71. K. Aotani, J. Electrochem. Soc., Japan, **21**, 180 (1953).
72. A. G. Russell, U.S. Pat., 1,960,029 (1934).
73. K. Aotani, J. Electrochem. Soc., Japan, **20**, 611 (1952).
74. S. Sklarew and L. Cinamon, U.S. Pat., 2,216,605 (1940).
75. S. A. Galva, Swiss Pat., 237,817, cl.76, (1945).
76. K. I. Vasu and T. L. Rama Char, J. Sci. and Ind. Research, **19B**, 413 (1960).
77. P. F. Hoglund and M. L. Holt, Trans. Electrochem. Soc., **88**, 359 (1945).
78. R. F. McElwee and M. L. Holt, J. Electrochem. Soc., **99**, 48 (1952).
79. T. F. Frantsevich-Zabludovskaya and A. I. Zayats, Trudy Chetvertogo Soveshchaniya po Elektrokhimi, Moscow, 524 (1956); Chem. Abs., **54**, 11753 (1960).