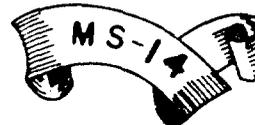




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THE ELECTRODEPOSITION OF CHROMIUM
A LITERATURE REVIEW

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BASIS METAL
(NICKEL)



CHROMIUM-IRON
ALLOY DEPOSITED

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CHROMIUM-IRON ALLOY ELECTRODEPOSIT

BY

CHARLES LEVY

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A LITERATURE REVIEW

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ABSTRACT

Methods for electrodeposition of chromium-base alloys have been reported in the periodical and patent literature. Sixty-seven references are reviewed. The principal alloying elements include iron, nickel, cobalt, tungsten, and molybdenum. Ternary alloys have also been reported. Although no outstanding advances have been made to date, it is anticipated that further research in this field will yield plating methods which are both practical and economical.

Interest in the electrodeposition of alloys has been intensified in recent years. This has, in general, been due to the more widespread use of electrodeposited coatings and to the failure of single metal deposits to yield the desired chemical and physical characteristics. In particular, coatings which exhibit good corrosion resistance at both ambient and high temperatures are much sought after.

The electrodeposition of brass has been practised in industry for over one hundred years. Currently, emphasis is centered on tin alloys,

The statements and opinions expressed herein are those of the author and do not necessarily indicate the views or the policy of the Army Ordnance Corps.

major advances having been made both here and in Great Britain. Pure chromium is known to have excellent resistance to most chemical agents, and, in particular, to oxygen up to 700°C (1). The difficulty with electrodeposited chromium, however, is that it contains an inherent structure of microcracks which extends through to the basic metal, allowing chemical attack. Dow and Stareck (2) have reported a crack-free chromium electrodeposit.

It is felt that the solution to the cracking problem in chromium plate lies in the development of methods to apply, relatively simply and economically, electrodeposits of chromium alloys. These deposits should possess chemical and physical properties which are equal, if not superior, to those of conventional chromium plate. An extensive literature survey has been undertaken to determine the methods already available. In a most thorough survey on alloy plating Faust (3), in 1940, made little reference to chromium alloy plating showing the lack of interest at that time. The principles of alloy plating have been well described by Blum and Hogaboom (4) and Faust (5). Most of the baths to be described are aqueous solutions. Fused salt baths in which a single metal alloy with cathode surface have not been considered, nor have the composite deposits of two or more metals, where the deposits are heat treated to form an alloy.

Chromium-Iron Deposits

The major portion of the work done on electrodeposition of chromium alloys has been concerned with alloys of chromium and iron. A number of investigators have reported that iron has little effect on deposits

obtained from conventional chromium trioxide plating baths. Alter and Mathers (6) stated that up to 50 g./l. of ferric iron did not affect the deposition of chromium, but higher concentrations did. In their study of throwing power in chromium plating baths, Farber and Blum (7) concluded that up to 2N ferric iron decreases the bright plating range and increases throwing power slightly. Kasper (8) found that only 0.10% iron deposited from a 2.5M chromium trioxide bath containing 1N ferric iron, and deposits made at 45°C. and 10 amp./sq.dm. were not bright. Addition of 25 g./l. ferrous carbonate produced negligible quantities of iron in the deposit, according to Gardam (9). Cassel (10), Schneidewind (11), Phillips (12), and Baker (13) also reported no iron in deposits from chromium trioxide baths.

Other investigators have reported that chromium-iron alloys can be deposited by making additions to chromium trioxide baths. Brenner, Burkhead, and Jennings (14) found that deposits containing 6-9% iron could be obtained from baths containing chromium trioxide, ferric dichromate, sulfate, and magnesium ions. Although the deposits contained up to 2.85% oxygen, the physical properties were inferior. Burr and associates (15) added ferrous sulfate to 4.0M chromium trioxide at sulfate ratios below 10:1 to produce deposits with up to 10% iron. Current efficiencies seemed to decrease with time of use of the solutions, apparently due to excessive build-up of trivalent chromium. The deposits, however, contained fewer cracks than conventional chromium plate.

Baths containing 1-2.5M chromium sulfate, 0.5M ferrous sulfate, and 0.005-1.0M sulfuric acid (to give a pH of 1.0 to 1.3) were reported by

Fuseya and Sasaki (16) to yield deposits of 16-65% chromium, 1-5% oxygen, balance iron. Current density was 74-139 amp./sq.dm. at 15°C. and current efficiency 14% or less. Hol'ts and Khariamov (17) also used mixed chromium and iron sulfates, to a total metal concentration of 1.6M, with a chromium to iron ratio of 1.5:0.1 moles. Current density was 10-15 amp./sq.in. and temperature 20-40°C. to yield an 80% chromium, 20% iron alloy. More recently, Yoshida and Yoshida (18) suggested use of a bath of 0.3M chromium sulfate, 0.3M ferrous sulfate, 2.2M ammonium sulfate, and 3.0M urea, at a pH of 2.4-2.8. Current density of 8-16 amp./sq.dm. gives a deposit containing 18-19% chromium. Baths of similar compositions have recently been patented by Yoshida (19).

A patent by I. G. Farbenindustrie A.-G. (Alexander Siemens, inventor) (20), claims a deposit of a chromium-iron alloy from a bath of 370 g./l. $K_2Cr_2O_7$, 250 g./l. chromium trioxide, 7 g./l. chromic oxide, and 80-100 g./l. ferrous sulfate. Safranek and Shaer (21) reported the physical properties of an unspecified electrodeposited chromium-iron alloy. Snavely, Faust, and Bride (22) claim deposition of a 94% chromium, 8% iron alloy which retains its hardness of 600-700 Knoop up to 1110°F. The bath composition is based on chromium and ferrous ammonium sulfates, sodium sulfite and magnesium and ammonium sulfates, at a pH of 1.7. Current density is 400 amp./sq.ft. at a temperature of 145°F. A patent issued to Safranek (23) claims deposition of a bright 85% chromium, 15% iron alloy on steel at 115°F. at a pH of 1.8-2.0 and a current density of 200 amp./sq.ft. The bath consists of 300 g./l. $CrNH_4(SO_4)_2 \cdot 12H_2O$, 150 g./l. $(NH_4)_2SO_4$, 5 g./l. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, and 0.5 g./l. methylpy-

ridinium chloride, the latter as a supplementary brightening agent. Fuseya and Sasaki (16), however, concluded that a chromium ammonium sulfate bath was not suitable for deposition of chromium since their results were poor. Lloyd (24) reports that alloys containing over 50% iron have been produced at low current efficiency, but gives no details. Finally, Lihl and Jenitschek (25) isolated a chromium-iron alloy at a mercury cathode.

Chromium-Nickel Deposits

As far back as 1894, Placet and Bonnet (26) claimed deposition of chromium-nickel alloys from solutions of chromium sulfate and nickel sulfate, acidified with sulfuric, phosphoric, hydrochloric, oxalic, or hydrofluosilicic acids. Dokras (27) has recently reviewed and discussed chromium-nickel codeposition. Krämer (28) added 1% nickel as oxide, hydroxide, carbonate, or a dicarboxylic acid salt to a chromium trioxide solution. Alter and Mathers (6) reported similar results with nickel as with iron, as did Cassel (10). Kasper (8) found that up to 1N Ni^{++} in a chromium trioxide bath had no effect on deposition of bright chromium. Additions of nickel dichromate to chromium trioxide baths yielded only a few tenths of a percent nickel in the deposits according to Brenner (14). Burr and associates (15) found that no satisfactory plates could be deposited from a nickel ammonium sulfate bath similar to that used for chromium-iron by Snavelly, Faust, and Bride (22). Starting with 4M solutions of chromium trioxide, nickel sulfate or nickel ammonium sulfate were added. Best results were obtained with a 10:1 CrO_3 to $SO_4 =$ ratio, the nickel being added as sulfate. However, only the bath containing chromium trioxide and nickel ammonium sulfate in a 5:1 ratio showed

nickel present in spectrographic analysis.

Skalozubov and Vlasova (29) electrodeposited a chromium-nickel alloy from a bath containing 250 g./l. chromium trioxide, 250 g./l. nickel sulfate, and 25 g./l. boric acid at a current density of 30-35 amp./sq.dm. and temperature 35-40°C. Ratios of chromium to nickel in the deposit can be varied by changing ratios of bath constituents and the chromium content increases with increasing current density. Wallace (30) claimed electroplating of a nickel-chromium alloy on steel using an alloy anode. The bath was made up of 32-96 oz./gal. nickel sulfate, 16-32 oz./gal. chromium carbonate, boric acid, and water. Yoshida and Yoshida (18) suggest that chromium-nickel alloys may be deposited in a similar manner to the method they used for chromium-iron alloys.

In 1953, Quaeley (31) deposited chromium-nickel alloys at a current density of 75-100 amp./sq.dm. at a temperature below 40°C. The bath composition included 200 g./l. chromium trioxide, 20 g./l. nickel chloride, and 5 ml./l. glacial acetic acid. The deposits were subsequently blackened by immersion in hydrochloric acid. The plating method was patented (32). Albin (33) claims a method for brush plating a chromium-nickel alloy. Two solutions were used, one containing nickel chloride, zinc chloride, ferric chloride, and water. The other has potassium chromate, hydrochloric and sulfuric acids, and water. The solutions are poured together at 25°C. and alternating current is passed as an activation treatment prior to use with a carbon rod anode and sponge. Varying compositions of chromium-nickel alloys were obtained by Natanson and Kozachek (34) from organosols in a two-layer bath. The aqueous solution contained NiCl_2 , CrCl_3 , NH_4Cl ,

urea, and HCl. The organic layer was composed of oleic acid and toluene. Again, Lihl and Jenitschek (25) have obtained chromium-nickel alloys at a mercury cathode.

Chromium-Cobalt Deposits

Adding up to 50 g./l. cobalt chromate to a chromium trioxide bath prevented deposition as reported by Alter and Mathers (6), while Brenner, Burkhead, and Jennings (14) state that cobalt dichromate additions yielded alloys inferior to conventional chromium plate. Humphries (35) patented electrodeposition of a cobalt-chromium alloy for razor blade edges. In 1923, Peffer and Pierce (36) patented a method for depositing chromium-cobalt from a solution of mixed sulfates or chlorides. Schulte (37) formed a plating bath by combining a portion of a solution of 50-75 parts cobalt sulfate, 30-40 parts sodium sulfate, 5-15 parts hydrofluoric acid and 250 parts water with a larger proportion of a solution formed from 75 parts chromium trioxide, 3 parts potassium hydroxide, 10 parts hydrofluosilicic acid, and 250 parts water. Yoshida and Yoshida (18) suggest that chromium may be alloyed with cobalt in a manner similar to iron. DuRose (38) suggests the addition of cobalt carbonate to a chromium plating bath composed of chromic acid and fluoboric acid to prevent anode sludge formation. Candussi (39) claims deposition of a chromium-cobalt alloy on steel or aluminum.

Chromium-Tungsten and Chromium-Molybdenum Deposits

Serious consideration has been given to the electrodeposition of chromium-tungsten and chromium-molybdenum alloys. Brenner, Burkhead, and Jennings (14) were not able to develop successful deposits by adding

tungsten or molybdenum in the form of complexes of phosphoric, hydrofluoric, or boric acid to chromium trioxide plating baths. Armstrong and Menefee (40) have patented a method which utilizes a tungsten carbide anode alloyed with chromium to yield an alloy deposit from an acidic aqueous solution of tungsten oxyfluoride. Another patent (41) sets forth addition to a tungsten oxyfluoride bath of an acid salt of the metal to be alloyed. The solution is maintained at a pH of 4.5-6.8, and a temperature of 35-80°C. Rogers and Burr (42) deposited chromium alloys with up to 30% tungsten from a solution of 2M chromium trioxide reduced to a trivalent chromium content of 40% with 300 g./l. ammonium citrate, and containing 150 g./l. tungstic anhydride. Deposits had excellent appearance and corrosion resistance, although appreciable (0.0001 inch) thicknesses could not be built up.

A method for electroplating chromium-molybdenum alloys has been patented by Ma (43). One to 30% molybdenum is obtained by dissolving molybdic anhydride to an aqueous chromium trioxide solution containing sulfuric acid. The use of a chromium-molybdenum alloy anode is preferred, at a current density of 15 amp./sq.dm. and temperature of 40°C. A plate 0.003 inch thick which contains 22.4% molybdenum will deposit in five hours. Shome (44) has deposited an alloy containing 1.7% molybdenum and 98.1% chromium which can be brightened by polishing. The bath composition was 360 g./l. H_2MoO_4 , 400 g./l. CrO_3 , and 4 g./l. H_2SO_4 at plating conditions of 40°C. and 1 amp./sq.in.

Miscellaneous Binary Chromium Deposits

Many other alloys of chromium have been under investigation.

Cassel (10), tried, in addition to iron and nickel, zinc, cadmium, silver, arsenic, and lead-mercury with poor results. Concentrations below 50 g./l. of copper, zinc, cadmium, vanadium, or aluminum, as well as ferric iron, nickel, or molybdenum did not affect deposition from the chromium trioxide bath, according to Alter and Mathers (6). Kasper (8) found that, although 1N zinc, cadmium, copper, or nickel had no effect on bright chromium plating baths, copper was found to be present to the extent of 0.08% in the deposit. Placet and Bonnet (26) claimed deposition of aluminum, magnesium, zinc, tin, antimony, silver, or platinum, as well as nickel and cobalt, as alloys of chromium. Marino (45) patented a method for deposition of an alloy of zinc, cadmium, aluminum, tin, cadmium, lead, antimony, nickel, cobalt or chromium by electrolysis of the tartrates, paratartrates, or oxalates of these metals in aqueous ammonia. Yoshida and Yoshida (18) suggest manganese as a codeposited metal for chromium, while Shaffer (46) added MnO_2 , $K_2Mn_2O_8$, $MnCl_2$, and Rochelle salts to CrO_3 plating baths.

A novel method for deposition of alloys including chromium has been patented by Cole (47). It consists in placing anodes of the metals to be alloyed at various distances from the cathode to form the desired alloy proportions. An apparatus is described in which the current for each electrode is separately adjustable. Rojas Chemical Works (48) has patented a bath which contains as a soluble aluminum compound 5-15% of the chromium trioxide content, calculated as aluminum hydroxide. Gardam (9) determined that 15-25 g./l. aluminum added as hydroxide produced negligible quantities of aluminum in deposits from chromium trioxide

baths. Up to 38.7 g./l. indium sulfate has been added to a conventional chromium plating bath by Hackerman (49,50), although indium was present to only a very small amount in the deposit. Rogers and Burr (42) could not achieve successful deposition of chromium-titanium alloys, but these compositions are claimed by Candussi (39) and Sugahara (51). The latter used an aqueous solution containing 250 g./l. CrO_3 , 2 g./l. H_2SO_4 , and 5 g./l. TiSiF_6 , at a current density of 30 amp./sq.dm.

Quaely (31,52), and Quaely and Lilliendahl (53), have patented a method for electrodeposition of a black chromium-vanadium alloy from an electrolyte containing 150-350 g./l. chromium trioxide and 2-10 g./l. vanadium as soluble halides, nitrates, or vanadates. Addition of 3-20 g./l. of acetic, formic, citric, oxalic, or propionic acid improved plating characteristics. Two baths patented by Rojas (54) contain zinc or barium. One composition is 400 g. chromium trioxide, 41-287.5g. zinc sulfate, and 12-81.4g. zinc oxide, with sufficient water for dissolution. The second bath, which was combined with the first to yield the final solution, contains 600g. chromium trioxide, 28-197.4g. barium carbonate, and 81.4g. zinc oxide. Greater throwing power than the conventional bath is claimed over wide ranges of current density and temperature. A more recent Rojas patent (55), claims improvement of chromium electrodeposition from zinc-containing baths similar to the aforementioned. Nickel or aluminum may be added in lieu of the zinc. Chromium in the quantity 0.01-40 g./l. is listed by Weiner (56) as an addition agent to a cadmium cyanide plating bath. Jennison and Bradley (57) claim a codeposit of tin with approximately 10% chromium. Patents covering the use of

strontium chromate and sulfate in chromium trioxide plating baths have been issued to Passal (58), Stareck (59), and Stareck and Dow (60).

Ternary Chromium Alloy Deposits

In 1940, Skalozubov and Goncharova (61) followed their work on chromium-nickel alloys by development of a chromium-trioxide, 250 g./l. nickel sulfate, 175 g./l. ferrous sulfate, and 25 g./l. boric acid. Optimum current density was 50 amp./sq.dm. at a temperature 60°C. Increase in current density caused an increase in chromium and a decrease in nickel and iron in the deposit. Raising the bath temperature decreased current efficiency and chromium content of the deposit. Frantsevich-Zabludovskaya (62) obtained chromium alloys with 2.8-7.75% molybdenum and 2.8-23.75% nickel. The bath composition was 320 g./l. chromium sulfate, 100 g./l. nickel sulfate, 100 g./l. ammonium molybdate, and 10 g./l. boric acid. The bath was pre-electrolyzed to contain 5-6% hexavalent chromium at a approximate pH of 2. With platinum anodes, the coating was bright and dense.

Ternary black chromium alloys were produced by Quaely (31,63) by adding 2-10 g./l. of vanadium as a soluble compound to the chromium-nickel bath previously described (32). Quaely and Lilliendaal (53) have patented another ternary alloy bath, the composition being 200 g./l. chromium trioxide, 80 g./l. nickel chloride, and 5 g./l. vanadium, which is dissolved in a minimum of nitric acid. Candussi and Lovantina (64) claim deposition of chromium hydride deposits from two baths, one containing nickel, ammonium, and cobalt sulfates, boric acid and water; the other, chromium trioxide, sulfuric acid, cobalt sulfate, and water.

A white brass coating has been patented by Fischer (65). A mineral acid and 25 g./l. chromium trioxide are added to a potassium cyanide bath containing zinc and copper. The current density is 1-5 amp./sq.dm. and the temperature 20-50°C. Fuchs (66) claims an electrodeposited alloy of 1-40% chromium, 1-40% tungsten and the remainder nickel. Finally, Neuendorff and Sauerwald (67) electrolyzed a fused chromite (58% Cr₂O₃, 15-17%, Fe₂O₃ MgO and Al₂O₃) with silicon dioxide. Using a carbon cathode, a deposit containing 39.5% chromium, 49.4% iron, and 7.3% carbon was obtained.

Although a considerable number of claims have been made, in practice it has generally been found that the chromium alloy deposit was either difficult to prepare, or it offered no substantial improvement over conventional chromium plate in physical or chemical characteristics. Judging from the success achieved in the alloying of bulk metals, there is no reason to expect less in the field of alloy coatings. It is anticipated that further research will yield plating methods which are both practical and economical.

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