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⑤④ **Method for brush electroplating, electrode and electrolyte therefore.**

⑤⑦ A brush electrode for use in electrotreating a metal surface, comprises an electrode (2) covered by an absorbent abrasive material (4) formed of synthetic fibres. A preferred abrasive material is a mixed polypropylene/nylon felt in which the fibres are consolidated by needle-punching and bonded with acrylic resin. The invention includes a method of depositing a metal or an alloy on to a metal body using the brush electrode, which allows good quality deposits to be obtained without the need to transport the metal body to a factory for the treatment. A solution for use in the method, which is especially stable under such conditions, includes metal ions which will form an alloy, a hydroxy-carboxylic acid such as a gluconate or heptonate to complex metal ions, and a carboxylic acid such as acetic acid also to complex metal ions. Best results are obtained when the pH of the solution is between 0.5 and 2.



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K 35/36ELECTROTREATING A METAL SURFACE**TITLE MODIFIED**
see front page

The invention relates to apparatus and chemicals useful in electro-treating a metal surface by a so-called brush technique. This technique may be used to electroplate or electro-clean a metal surface. The metal surface may be the die surface of a forging or pressing tool, a printed circuit, a printing roller, an aircraft component or the like. The deposit may be put on to increase resistance to wear or to corrosion or both. For convenience and brevity this system will be called collectively "brush plating".

It has been known for many years to electroplate metal deposit on to metal engineering components to increase their useful life. One method of electroplating involves immersing the component in a bath containing a solution of the metal ions to form a deposit of metal or alloy, the so-called vat or bath plating technique. This method cannot be used to plate large metal bodies such as metal-forming dies, or components of ships and aircraft which cannot be easily transported to an electroplating plant.

Another method involves applying a plating solution to the metal body by means of a brush anode with the metal body acting as the cathode to deposit a coating from the solution on to the metal body. The brush comprises an electrode having a stylus portion covered by an absorbent material such as soft cotton wool and in use the stylus is moved over the

surface to be plated. This technique became industrial in the 1950's, see e.g. M. Rubinstein, "Brush plating now practical" Materials & Methods (1954) 40 6-8. Brush plating started as a means of repairing defective areas of a vat plated metal surface and it has been adopted commercially for plating in situ large components of ships and aircrafts and fixed items such as statues and roofs. While the absorbent cotton wool functions quite well as an absorbent material, it can cause electrical problems and the cotton wool fibres can be released to be included in the plated deposit. The solutions used in brush electroplating are subjected to much more severe operating conditions than those of bath electroplating techniques. For example, the brush electroplating solutions are subjected to high and variable current densities, which can give rise to localised boiling of the solution, and they may also be subjected to large variations in pH due to localised loss of metal ions from the solution. While conventional bath electroplating solutions have been tried for use in brush electroplating, they are generally unsuitable due to their inability to form a coating having a sufficient thickness and where relevant a suitable content of alloy.

It is an object of this invention to improve a brush plating technique by providing a brush of improved structure the use of which enables plating to be done efficiently and yields a plating of improved quality. In addition it is an object of the invention to provide a plating solution especially adapted for use in a method of brush plating.

According to a first feature of the invention there is provided a brush electrode for use in contacting the surface of a metal part to be treated such as the surface of a metal forming tool with a treating solution, comprising an electrode having a stylus portion adapted to hold treating solution, in which the stylus portion includes an absorbent abrasive material.

By virtue of its abrasive nature when the absorbent material is

brushed over the metal surface being plated, surface irregularities in the plating are rubbed away as they form so giving the plating a uniform and smooth finish. This uniformity and smoothness can be obtained even when the brush is used by unskilled operatives. In addition, the plating rate is also improved.

Preferably the absorbent abrasive material is formed of synthetic fibres. With such fibres the material can have a large internal volume which gives the material the ability to absorb a large quantity of the treating solution. Synthetic fibres tend to be inert to the acids and heat of the treating solution. Fibres which are angular in shape are much preferred since they tend to be more abrasive. The fibres may be held together in any convenient way; it is preferred to consolidate them by needle punching and binding them by resin. A preferred absorbent abrasive material is a mixed polypropylene/nylon felt bonded with acrylic resin.

Preferably the material has a fibre density of between 400 g/sq.m. and 1000 g/sq.m. to allow a satisfactory amount of the solution to be absorbed. The thickness of the fibrous material covering the electrode is preferably between 0.2 mm and 15 mm.

The absorbent abrasive material may also be used with other suitable materials. The felt may be located on top of a cotton gauze located about the electrode.

The absorbent abrasive material may be held to the electrode by any convenient means such as bands or straps. It is usual to hold the material on to the stylus end of the electrode which however may be shaped, e.g. recessed, to receive the material.

The electrode used in brush plating is typically inert. The electrode may be formed of inert material such as platinum or platinum

alloys, stainless steel or carbon; high purity high density carbon is preferred.

The brush electrode of the invention may be used to apply as a treating solution an electrocleaning solution or an electroplating solution. In the former case the electrode will be cathodic and the treating solution will typically include dilute mineral acids and in the latter case the electrode will be anodic.

According to another aspect of the invention, there is provided a method of brush electroplating a metal surface, comprising connecting the metal surface to the negative pole of a direct current or rectified alternating current power source, wetting a brush electrode of the invention with an aqueous acidic solution containing metal ions which will form a deposit of a metal or an alloy, connecting the brush electrode to the positive pole of the power source, and applying the wetted electrode to the surface of the metal body to make an electrical circuit and deposit the alloy on to the metal body.

The metal ions present in the solution may be adapted to deposit a metal or an alloy on the metal surface being plated. It is preferred for wear-resistance that the ions form a deposit of a binary or a ternary alloy. Examples of binary alloys which have been deposited by the method of the invention include cobalt-molybdenum which has been deposited with a molybdenum content of about 8% or more and cobalt-tungsten which has been deposited with a tungsten content of up to about 19%, both alloys being deposited in a coating thickness of up to about 30 μm . Examples of other binary alloys which may be deposited by the method are nickel-molybdenum, nickel-tungsten, iron-molybdenum and iron-tungsten, and examples of ternary alloys are iron-nickel-molybdenum and cobalt-tungsten-molybdenum. The metal ions are usually presented as water-soluble salts, and the concentration depends on the particular salt used. In the case of cobalt sulphate the concentration

can be between 100 g/l and saturation and is usually between 150 and 600 g/l. In the case of sodium molybdate the concentration can be between 1 g/l and 100 g/l, and is usually between 3 g/l and 50 g/l. Sodium tungstate may be used at the same concentration as the sodium molybdate or in a higher concentration.

It is much preferred to include in the solution both a hydroxy-carboxylic acid and a carboxylic acid to complex metal ions if brush plating of a deposit of an alloy is to be at a satisfactory industrial rate.

The hydroxy-carboxylic acid may have from 2 to 8 carbon atoms, from one to six hydroxyl groups and from one to three carboxyl groups. This material may also be presented to the solution as a water-soluble salt. Preferably the hydroxy-carboxylic acid has the general formula $C_nH_{2n}O_{n+1}$ where n is an integer from 2 to 8. Gluconates and heptonates are particularly suitable materials. The concentration in which the hydroxy-carboxylic acid is present in the solution may be from 50 g/l to 800 g/l but for best results the concentration should be between 100 g/l and 400 g/l.

The presence of carboxylic acid serves to increase the maximum usable voltage and the current density which increase the rate of plating, and in addition its presence increases the resistance of the deposited alloy to cracking. The concentration of the carboxylic acid may be as low as 10 g/l and the maximum concentration is about 100 g/l, above which the plating efficiency falls. Mono-, di- or tri-carboxylic acids may be used and they may be presented to the solution as a water-soluble salt. Mixture of suitable materials may be used. Acetate and formate have proved to be effective.

The plating solution preferably has a pH of below about 4, most preferably below 3, since plating efficiency tends to fall if the pH

is above this value. Best results are obtained within the pH range of 0.5 to 2. A plating solution as made up may have a pH value outside this range, in which case acid or alkali may be added as appropriate to reach the desired value.

It is preferred to form a plating of about 5 to 30 μm thick. In practice the coating is preferably at least 10 μm thick.

The operating voltage may range from 10 to 35 volts, preferably 18 to 20 volts. The higher operating voltages are preferred if a higher content of molybdenum is required in the deposit.

One example of the invention will now be described with reference to the accompanying diagrammatic drawing which is a side view of a brush electrode for use in the method.

The brush electrode comprises a handle 1 to one end of which is secured a carbon electrode 2 shown in ghost outline. The handle 1 is of an electrical insulating material and a wire 3 passes from the electrode 2 through the handle 1. A felt 4 covers the electrode 2 and is held on to the brush by an elastic band 5. The felt 4 is 5 mm thick.

The felt was formed of 75% polypropylene fibres and 25% nylon fibres which were consolidated by needle punching to a density of about 580 g.m^{-2} . The consolidated felt was then dipped in acrylic resin which was then heat cured to bond the fibres together. The nylon fibres were of trinodular shape and the polypropylene fibres of rectangular shape. The formed felt was then located on the electrode 2 and held there by the band 5.

In use the wire 3 is connected to one pole of a suitable power source and a metal body to be coated is connected to the other pole.

When coating the body by the method of the invention, the electrode is connected as the anode and the metal body is connected as the cathode. The brush electrode may also be used for cleaning or etching of the metal body in a known manner prior to plating, to give the body a surface which is better able to be coated, in which cases the electrode is connected as the cathode.

The following Example illustrates how the brush electrode may be used in the method of the invention.

EXAMPLE 1

An aqueous solution was made by dissolving the following in water

cobalt sulphate $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	600 g/l
sodium molybdate	25 g/l
sodium heptonate	200 g/l
glacial acetic acid	42 g/l

This gave a solution having a pH of about 3.5 which was then adjusted to a value of about 1.0 by addition of mineral acid.

A pre-cleaned tool die was connected to the negative pole of a rectified alternating current power source giving about 20 volts. The brush electrode was connected to the positive pole of the power source. The tip of the brush electrode was then dipped into the plating solution so that the felt absorbed the solution, and the wetted electrode was then brushed over the tool die. The amount of material deposited was monitored by means of an ampere-hour meter connected in the circuit. The brush was kept moving, and was always kept wet with the solution.

An area of one square decametre was coated to a thickness of about $1 \mu\text{m}$ in about 2 minutes. The actual coating rate obtained

depends upon the size of the brush electrode and operator skill, however, no problem was encountered in producing a coating of more than 12 μm thick. On analysis, the coating was found to be a cobalt-molybdenum alloy containing between 6% and 12% molybdenum. The coating was characterised by a very fine grain size, a low coefficient of friction and a satin finish. The presence of the coating extended the life of the die significantly.

Example 2

The solution of Example 1 was made up using 50 g/l of the molybdate and the pH adjusted to 1.5 and similar good results were obtained.

The method of the invention makes it possible for an operator to travel from site to site doing coating jobs using portable apparatus.

The plating solution is stable under long-term storage conditions and is not susceptible to contamination or burning during brush plating. The quality of the coating obtained by the method is at least as good as those obtained by bath electroplating techniques, and good quality coatings will be obtained despite the variations in solution pH and operating voltages typical of industrial practice.

The metal surfaces to be plated by the method of the invention will typically be of metal forming tools. Such tools may be dies and moulds and include hot forging dies and cold pressing tools. In a series of field evaluations plating different tools using the brush electrode and solutions of the invention, it was observed that when plating the tool surfaces to produce a cobalt-molybdenum alloy plating about 12 μm thick, there was an average increase in die life of 60% for press tools and 50% for drop hammer dies. In the case of a hot forging die it was further noticed that the metal being formed flowed more easily over the die surface and as a result the forging temperature could be lowered giving additional saving on energy costs. In the case of cold pressing tools,

bits of metal from the metal being formed in the tool are left on the die surface and this metal pick up must be removed by hand polishing if the surface of metal being formed in the tool is not to be scored and otherwise damaged. This metal pick up is removed from time to time and the tool is then out of commission before it can be reused. In the case of plated dies it was found that there was a decrease in the time for which they were out of commission of about 78% compared to unplated tools. In addition a plated die needs little or no lubrication compared with an unplated die so saving labour in applying lubricant and also in cleaning the lubricant off at a later stage.

In all the field trials quoted above the plating was done on site in a plant or factory without removing the tool to a plating bath and so these improvements were obtained without transport costs and loss of tools to the plant for prolonged periods.

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CLAIMS :

1. A brush electrode for use in electrotreating a metal surface, such as the surface of a metal forming tool, comprising an electrode having a stylus portion adapted to hold and apply a treating solution to electrotreat the metal surface,
characterised in that the stylus portion includes an absorbent abrasive material (4).
2. A brush electrode according to Claim 1, in which the absorbent abrasive material (4) is formed of synthetic fibres.
3. A brush electrode according to Claim 2, in which the fibres are angular in shape.
4. A brush electrode according to Claim 2 or Claim 3, in which the fibres are held together by consolidating them by needle punching and binding with resin.
5. A brush electrode according to Claim 4, in which the absorbent abrasive material is a mixed polypropylene/nylon felt bonded with acrylic resin.

6. A method of electrotreating a metal surface, comprising connecting the metal surface to the negative pole of a direct current or rectified alternating current power source, wetting a brush electrode with an aqueous acidic solution containing metal ions which will form a deposit of a metal or an alloy, connecting the brush electrode to the positive pole of the power source, and applying the wetted electrode to the surface of the metal body to make an electrical circuit and deposit the metal or alloy on to the metal body,

characterised by applying to the metal surface by a brush electrode according to any one of Claims 1 to 5, an aqueous solution having a pH below 4 for sufficient time and at a sufficient voltage to build up on the metal surface a deposit of metal or metal alloy at least 10 μm thick.

7. A method according to Claim 6, in which the solution includes a hydroxy-carboxylic acid and a carboxylic acid to complex metal ions.

8. A method according to Claim 6 or Claim 7, in which the solution has a pH of between 0.5 and 2.0.

9. A method according to any one of Claims 6 to 8, in which the deposit is built up to a thickness of between 10 μm and 30 μm .

10. A method according to any one of Claims 6 to 9, in which the metal surface to be electrotreated is part of a metal forming tool located in a metal forming factory.

11. A metal surface having deposited thereon a metal or metal alloy,

characterised in that the metal or metal alloy has been deposited by a method according to any one of Claims 6 to 10.

12. An aqueous acidic solution for use in electrotreating a metal surface, containing metal ions which will form a deposit of a metal or an alloy,

characterised by the presence of both a hydroxy-carboxylic acid and a carboxylic acid, the solution having a pH below 4.

13. A solution according to Claim 12, in which the pH of the solution is between 0.5 and 2.0.

14. A solution according to Claim 12 or Claim 13, in which the hydroxy-carboxylic acid has from 2 to 8 carbon atoms, from one to six hydroxyl groups and from one to three carboxyl groups.

15. A solution according to any one of Claims 12 to 14, in which the hydroxy-carboxylic acid is gluconate or heptonate.

16. A solution according to any one of Claims 12 to 15, in which the hydroxy-carboxylic acid is present in a concentration of between 50 g/l and 800 g/l and the carboxylic acid is present in a concentration of between 10 g/l and 100 g/l.

17. A solution according to any one of Claims 12 to 16, in which the metal ions are selected to form a cobalt-molybdenum or a cobalt-tungsten alloy.

18. A solution according to any one of Claims 12 to 16, in which the metal ions are selected to form a nickel-molybdenum, a nickel-tungsten, an iron-molybdenum, an iron-tungsten, an iron-nickel-molybdenum or a cobalt-tungsten-molybdenum alloy.

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 3 725 214 (BRIDE)</u> * Column 2, lines 7-35; column 6, lines 10-17; claims 1-4 * --	1,2,6,7,8,10	C 25 D 5/06 3/56
	<u>FR - A - 2 176 036 (SIFCO)</u> * Page 4, lines 27-35; page 8, lines 14-28; claims 1-21 * --	1,2	
	<u>US - A - 4 067 781 (RAPIDS)</u> * Column 3, lines 25-35; claims 1-4 * --	1,2	
	<u>SU - A - 180 453 (PILLE)</u> * Whole patent * --	1,6,8,9,10	TECHNICAL FIELDS SEARCHED (Int.Cl. ²)
	<u>DE - A - 2 333 069 (OXY)</u> * Pages 26-28; claim 1 * --	7	C 25 D 5/06 3/56
	COBALT 1975, 1, pages 17-28 DENNIS et al. "The use of electro-deposited cobalt alloy coatings to enhance the wear resistance of hot farging dies". ----		CATEGORY OF CITED DOCUMENTS
The present search report has been drawn up for all claims			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons &: member of the same patent family, corresponding document
Place of search	Date of completion of the search	Examiner	
The Hague	27-04-1979	VAN LEEUWEN	