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2,717,870

ELECTRODEPOSITION OF MANGANESE

Reginald S. Dean, Washington, D. C.

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This invention relates to the electrodeposition of manganese can be electrolytically deposited at high current densities. It has for its aim the provision of electrolytic baths from which manganese can be deposited in a single compartment cell, and from which a considerable amount of manganese may be deposited in such a cell without replenishment.

In the known art, manganese has been deposited from electrolytes which gave satisfactory deposits only within a very limited pH range, namely 7.5–8.5. In order to deposit any substantial amount of manganese without departing from the permissible pH range, two compartment cells have been almost exclusively used. In other instances, attempts have been made to main the required pH of the solution in a single compartment cell by the use of soluble anodes. Such attempts, however, have not been successful because of oxidation or chemical attack on the anode. Further the manganese deposits made in accordance with the known art have been lacking in ductility and brightness, which properties are desirable for many purposes.

I have found that all of these difficulties can be overcome by the use of baths containing manganese ammonia complexes having the manganese predominantly in the anion, such complexes being maintained in an aqueous solution containing at least six moles per liter of NH_3 . The manganese content of such baths may be from ten to one hundred grams per liter, and the anion may be any anion forming a more soluble manganese salt than manganese sulphate. The preparation of solutions containing these manganese ammonia complexes is described more fully in my co-pending application Serial Number 57,376 dated October 29, 1948, now Patent No. 2,608,463. For the purposes of the present invention, baths containing the manganese ammonia complex with manganese in the anion may be made by any of the following processes: (1) The solution of a soluble manganese salt such as the sulphate or chloride in relatively concentrated aqueous ammonia; (2) the solution of manganous oxide in an aqueous solution containing an ammonium salt of the desired anion and from six to seventeen moles per liter of NH_3 ; (3) the solution of metallic manganese in an aqueous solution of an ammonium salt of the desired anion and the addition of gaseous ammonia to such solution to bring the concentration of the ammonia up to at least six moles per liter. The pH of the solutions prepared in this way is from 9.0–10.5 and is only slightly changed by changing the manganese concentration, that is to say, the solutions are very strongly buffered and large changes in the concentration of both manganese and the original anion may be made without changing the pH. As a result of this strong buffering electrolysis may be carried on to remove as much as thirty grams per liter of manganese from some of the solutions in a single compartment cell without significantly changing the pH or plating conditions for the solution.

The solutions may be replenished by the addition of manganese metal or manganous oxide. A soluble man-

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ganese anode may also be used to replenish the solution but in this case the current density at the anode must be maintained below about 20 amperes per square foot above which oxidation takes place. If an insoluble anode is to be used, it should be one having a minimum tendency to oxidize manganese. Such anodes are those used in the known process for electrowinning manganese, such as lead containing one percent silver and preformed to provide an adherent coating of lead and manganese oxide. The conditions for such preforming are set forth in U. S. Patent No. 2,439,805 dated April 20, 1948. This anode and the alloy of lead-tin-cobalt are suitable for sulphate baths, for other baths graphite or magnetite should be used.

The cathodes which may be used in the practice of this invention are very much more diverse than those which may be used in the known art. The limiting factor in the selection of a cathode material is its chemical attack by the electrolyte, since most metals are not attacked by the ammoniacal baths of this invention all metals may be used as cathodes which are at least as noble as magnesium. The manganese is deposited from the baths of this invention entirely in the gamma or ductile form. It may be preserved in this form by the addition of from .05–.25 gram per liter of copper in the electrolyte. The co-deposition of manganese and copper takes place readily from the baths of this invention. When plating on a copper cathode there is always sufficient solution of the copper to provide a permanently ductile deposit.

The current density for plating manganese from the baths of this invention depends upon the type of plate desired, and upon the specific anion used in making the solution. All of the baths yield bright plates at high current densities. Broadly current densities of at least 100 amperes per square foot are required to obtain efficient plating from the baths of the invention. To obtain bright plates requires from 100–1,000 amperes per square foot current density. The electrolytes which give bright plates at lower current densities, namely, 100–300 amperes per square foot are those in which the original anion is somewhat complex. To this class belong solutions made from alkane sulphonates, sulphamates and fluoroborates. When the simple anion constituent of the bath is the chloride or sulphate, the current density is maintained at 600–1000 amperes per square foot, whereby to obtain a bright plate.

In carrying out the electrolysis according to the principles of the present invention the temperature of the electrolyte is to be maintained below 45° C.

Having described my invention in general, I will now illustrate it with specific examples.

Example I

I take sixty grams of electrolytic manganese and dissolve it in 1 liter of solution containing two hundred grams of ammonium sulphate, and fourteen moles of ammonia. I stabilize this solution against oxidation in air by adding 0.1 gram hydroxylamine acid sulphate. I electrolyze this solution in a single compartment cell using an anode of lead containing one percent silver, which has been coated with an oxide film by making it an anode in a solution containing .125 gram per liter ammonium sulphate, and 16 grams per liter manganese at a pH of 5.0. The cathode is a sheet of titanium. I carry on the electrolysis at 300 amperes per square foot. A matte plate of ductile manganese is obtained which may be readily stripped from the cathode and becomes brittle in about twenty-four hours at room temperature. In this and the following examples a temperature within the range 20–45° C. was maintained.

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Example 2

I proceed as in Example 1, except that I use a copper cathode. The plate is adherent and is permanently ductile.

Example 3

I proceed as in Example 2, except that I raise the current density to 1,000 amperes per square foot. The resulting plate is bright and permanently ductile. When plating at high current densities, I cool the solution by circulating it over glass tubes carrying iced brine. A temperature of about 35° C. is the best temperature for plating.

Example 4

I make a solution by dissolving 50 grams of pure manganous oxide in one liter of a solution containing 260 grams of alkane sulphononic acid, molecular weight 120 and 10 moles per liter of ammonia. I filter this solution to remove any undissolved material. I then add 0.1 gram per liter hydroxylamine acid sulphate. I electrolyze this solution in a single compartment cell using a graphite anode and a copper cathode. I carry on the electrolysis at 200 amperes per square foot and obtain a bright ductile plate.

Example 5

I proceed as in Example 4, except that I carry on the electrolysis at 1,000 amperes per square foot. The plate is bright and permanently ductile.

Example 6

I take the solution as prepared in Example 4 and add 0.25 gram per liter copper sulphate. I carry on the plating as in Example 4, except that I use a steel cathode. I obtain a bright adherent, permanently ductile plate.

Example 7

I take the solution as prepared in Example 4 and electrolyze it, using a copper cathode and an electrolytic manganese anode. The current density at the cathode is 200 amperes per square foot. At the anode it is 10 amperes per square foot. The solution is cooled by passing over glass tubes containing iced brine. Electrolysis is continued until a plate 1/8 inch thick is obtained. This plate is permanently ductile. The current efficiency for deposition is 88 percent, and for solution of the anode, 89 percent.

Example 8

I make a solution by dissolving 71 grams per liter of manganous oxide in 1 liter of solution containing 1 mole of ammonium sulphamate and 10 moles of ammonia. I add 0.1 gram hydroxylamine to this solution. I electrolyze the solution, using a graphite anode and a copper cathode, in a single compartment cell. I pass the solution through the cell at such a rate that 30 grams per liter of manganese is removed. I then replenish the solution by adding manganous oxide and returning the solution to the cell. The plating conditions are current density 100 amperes per square foot, temperature 35° C., current efficiency 86 percent, nature of deposit smooth and ductile.

As is disclosed in Patent No. 2,608,463, in solutions

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containing the above-described manganese ammonia complexes, having the manganese predominantly in the anion, the acid anion present may be that of hydrochloric, acetic, nitric, sulphuric, perchloric, boric, naphthenic, benzoic, cinnamic, hydrosulphuric, carbonic, carbamic, dithionic, fluoboric, alkane sulphononic, phenolsulphononic, fluosilicic, succinic, lactic, hydroxyacetic, thiocyanic or sulphamic acid. As pointed out in said patent, the amount of acid anion present shall be at least the stoichiometric equivalent of the amount of manganese present in the solution.

What is claimed is:

1. The method of electro-depositing a smooth bright plate of manganese which includes the steps of passing a unidirectional current between an anode and an insoluble cathode in a single compartment cell containing as the electrolyte an aqueous solution having a composition of 10-50 grams per liter Mn, 6-17 moles per liter NH₃ and a simple anion forming a salt with manganese at least as soluble as manganese sulphate, in an amount at least stoichiometrically equivalent to the amount of manganese present in the solution, said solution being strongly ammoniacal and having a pH of 9.0-10.5 and the manganese being predominantly in the anion, the current density at the cathode being 100-1,000 amperes per square foot and the current density at the anode being less than that at the cathode, and maintaining the temperature of said electrolyte below 45° C.

2. The process of claim 1 in which the simple anion in the electrolyte is selected from the group consisting of sulphamate and alkane sulphonate, and in which the current density is maintained in the range 100-300 amperes per square foot, whereby to obtain a bright plate.

3. The method of claim 1 in which the simple anion constituent of the bath is the sulphate and the current density is maintained at 600-1000 amperes per square foot, whereby to obtain a bright plate.

4. The method of electrodepositing manganese in a single compartment cell which consists in passing a unidirectional current from a metallic manganese anode to an insoluble metallic cathode in an electrolyte containing per liter 10-50 grams Mn, 6-17 moles per liter NH₃, and the anion selected from the group consisting of sulphamate and alkane sulphonate, said anion being present in an amount at least the stoichiometric equivalent of the amount of manganese present in the electrolyte, said electrolyte being strongly ammoniacal and having a pH of 9.0-10.5, and the manganese being predominantly in a complex anion, maintaining the current density at the anode at less than 20 amperes per square foot and the current density at the cathode at 100-300 amperes per square foot, the temperature during electrolysis being maintained from 20-45° C.

References Cited in the file of this patent

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