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ELECTRODEPOSITION OF MANGANESE AND CATHODE THEREFOR

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This invention relates to a cathode for use in the electrowinning of manganese and other purposes and to a process of using said cathode.

Some of the requirements which must be met by a successful cathode for the electrodeposition of manganese, particularly in the electrowinning of manganese from solutions prepared from manganese containing ores will be stated as follows:

1. It is necessary to use some substance other than manganese as this metal is too brittle to be used as such.

2. That substance must be one from which the deposited manganese can be readily separated, e. g., by flexing, bending, hammering, etc., preferably by flexing. Therefore the cathode must be strong, tough, and resilient and not readily subject to permanent deformation.

3. The cathode must be of such a nature that the manganese will adhere thereto during electro deposition but will readily part or separate therefrom, completely, after the deposition is completed, by any of the mechanical operations above mentioned. If portions of the manganese adhere to the cathode so firmly as to require laborious mechanical operations for their removal or any extensive chemical treatment, the cathode is unsatisfactory for successful commercial operation.

4. The cathode must be so inert that it will not be affected by cleaning compounds so as to form a "rust" or deposit which would contaminate the electrolyte or interfere with the manganese deposit.

5. The cathode must be so inert that if any manganese adheres thereto as a residue after the removal of the cathodic deposit as a whole, said residue may be readily removed by a simple chemical treatment without corroding or otherwise impairing the surface, so that a simple buffing operation will restore the surface to a condition which permits of another plating cycle and subsequent easy removal of the manganese.

6. The surface of the cathode should be capable of receiving a high polish.

7. The cathode must be sufficiently resilient to permit flexing without permanent deformation, and sufficiently free from stresses so that it does not warp.

8. One of the fundamental purposes of obtaining metallic manganese by the electrowinning process, as distinguished from other methods, is to obtain the manganese in a state of high purity and to this end the electrolytes are prepared in a condition of high purity in respect of metals that would cause contamination. There-

fore the cathode must be so inert that it will not cause any contamination of the electrolyte or direct contamination of the manganese deposit. More specifically, the cathode must be sufficiently inert so that substantially no corrosion is caused by galvanic or other action at the solution line.

9. The effective life of the cathode, i. e., the time during which it will meet the above requirements, must be at least 5,000 hours.

These requirements and the difficulty of meeting them have created a problem. Numerous unsuccessful efforts have been made, prior to this invention, to solve that problem.

It is an object of this invention to solve that problem and to thereby provide a successful cathode adapted for the deposition of manganese, particularly in the electrowinning thereof, and other metals.

It is a further object to provide a process of making said cathode, to improve its desirable characteristics and performance.

It is a further object to provide a process of using said cathode for the deposition of manganese and other metals.

An understanding of the invention will be assisted by a brief resume of some of the unsuccessful efforts to solve the problem which forms the background of the invention.

In the electrowinning of manganese, the cell is divided into two compartments, a catholyte chamber and an anolyte chamber, separated by a permeable membrane. Both chambers contain a suitable manganese salt usually manganese sulphate and usually ammonium sulfate. Owing to electrolysis, the pH of the catholyte may be about 6.5 to 8.0 and that of the anolyte 0.5 to 1.5. The concentration of manganese, as sulphate may be 25 to 35 grams per liter in the catholyte chamber and from 15 to 25 grams per liter in the anolyte chamber. Each chamber may contain about 120 to 170 grams per liter of ammonium sulphate.

The unsuccessful efforts reviewed below were made under comparable conditions in catholytes within the above concentrations. The cathode in each case was a metallic sheet measuring about 18 by 36 inches immersed in the catholyte to a depth of about 30 inches.

First, cold rolled steel was used during a period of 48 hours. The cathode was then removed and an attempt made to remove the manganese deposit by flexing, bending and hammering. Not only was it almost impossible to remove the deposit but, on analysis, the deposit when finally removed was found to contain 0.1 percent of iron.

which was much beyond the saleable limit for electrolytic manganese. After various treatments including buffing, grinding, oiling and "passivating" (treatment with dilute bichromate solution) of the steel surface, it was possible to get a surface from which the manganese could be more readily removed but this treatment did not overcome corrosion and contamination of the catholyte. Corrosion products formed on the surface of the cathode exposed to air, dropped into the catholyte and introduced iron salts which contaminated the electrolyte and the deposit. Etching of the cathode at the electrolyte air junction also occurred and caused contamination of the electrolyte and the manganese deposit.

Copper, lead, tin and tin plate were tried. All of these caused serious contamination of the electrolyte and of the manganese deposit and the tin coating peeled off with the manganese deposit. Serious contamination was also caused by Monel metal, pure nickel and "18-8" alloy (18% chromium, 8% nickel and the balance iron).

The iron alloy containing 17 percent chromium was satisfactory for about 480 hours of cyclic use which was much too short to be economical. At the end of this period it was so badly etched that the manganese could not be satisfactorily removed therefrom on further use.

The noble metals were too expensive either as such or in the form of coatings. Cold rolled tantalum was also too expensive and not sufficiently inert.

Iron alloys containing 18 percent chromium and 12 percent nickel and the balance iron and those containing 24 percent chromium and 18 percent nickel and the balance iron were also found to be unsatisfactory.

It was finally discovered that austenitic alloys illustrated by the composition 18 percent chromium, 12 percent nickel, 2 to 4 percent molybdenum and the balance iron provided means for a solution of the problem.

In accordance with this invention, an alloy having a composition within the limits chromium 17 to 19 percent, nickel 11 to 13 percent, molybdenum 2 to 4 percent and the balance iron is first annealed to remove stresses and eliminate warping. It is then surface hardened by cold working, e. g., by grinding the surface with 80 mesh grit. This imparts resilience. The sheet can then be cold rolled without substantially altering the dimensions and is cold rolled in order to produce a planar surface, smooth out grinding marks and further work-harden the sheet. After this is done, the sheet is polished and then possesses a combination of properties meeting the above listed criteria. The hardening operations, e. g., surface grinding and cold rolling, are continued until the desired degree of resilience is imparted, i. e., until the sheet is sufficiently resilient and elastic to be capable of temporary deformation to remove the metallic deposit such as flexing, for example, without permanent deformation.

The process of using the cathode of the present invention may be illustrated as follows; this process being a cycle which is continuously repeated.

The cathode is placed in the cathode chamber and manganese is deposited thereon. The cathode and its adhering manganese deposit is then removed, washed to remove electrolyte and dried as for example in a current of hot air, the washing step being preferably preceded by treatment with a dilute bichromate solution to passivate the deposit and prevent oxidation during drying. The cathode and manganese deposit is then ma-

nipulated to remove the manganese as for example by bending or flexing over a curved surface. If any residual manganese scrap remains on the cathode, it is removed by treatment with dilute mineral acid, e. g., 3 per cent sulphuric acid or other suitable solvent and then washed with water to remove the solvent. Instead of treatment with an acid or other solvent, said residual manganese may be removed electrolytically. This may be done by employing the cathode with residual adherent manganese as an anode in an alkaline electrolyte, e. g., 5 per cent K_2CO_3 and lead as a cathode or in an acid electrolyte, for example, anolyte such as employed in manganese electrowinning. Dirt and grease are then removed, as for example by treatment with a suitable emulsifying agent, e. g., soap, soda ash, trisodium phosphate, sulfonates, salts of sulfated alcohols, etc., and other detergents or by known methods of electrolytic cleaning. It is then buffed and polished, as for example by the application of high speed cotton buffing wheels and a buffing compound containing wax or the like and a chromium oxide powder known in the trade as "green rouge." It is then treated with an organic solvent to remove the buffing compound and is ready for another cycle of use in the electrolytic cell.

I claim:

1. A cathode adapted for the electrolytic deposition of a brittle metal thereon and the ready removal of said deposit therefrom, said cathode being in sheet form, having a substantially planar surface, sufficiently free from stresses to prevent warping, sufficiently resilient to permit flexing without permanent deformation, sufficiently inert to prevent substantial contamination of the electrolyte and manganese deposit, said cathode being an annealed, surface ground, cold rolled and surface polished alloy having the composition; chromium 17 to 19 per cent, nickel 11 to 13 per cent, molybdenum 2 to 4 per cent and the balance iron.

2. A cathode adapted for the electrolytic deposition of a metal thereon and the ready removal of said deposit therefrom, said cathode being in sheet form, having a substantially planar surface, sufficiently free from stresses to prevent warping, sufficiently resilient to permit flexing without permanent deformation, sufficiently inert to prevent substantial contamination of the electrolyte and manganese deposit, said cathode being an annealed surface ground, cold rolled and surface polished alloy having the composition; chromium 18 per cent, nickel 12 per cent, molybdenum 2 to 4 per cent and the balance iron.

3. The process of making a cathode adapted for the electrolytic deposition of a metal thereon and the ready removal of said deposit therefrom which comprises providing an alloy in sheet form having the composition; chromium 17 to 19 per cent, nickel 11 to 13 per cent, molybdenum 2 to 4 per cent, and the balance iron, annealing said sheet, hardening the surface thereof and cold rolling said sheet, until a resilience is imparted thereto sufficient to permit flexing for the purpose of removing a brittle metallic deposit therefrom, and imparting a surface polish.

4. The process of electrolytically depositing manganese on a cathode, removing said deposit therefrom and conditioning the cathode for a subsequent deposit which comprises electrolytically depositing a metal from an aqueous solution of a salt of said metal on a cathode in sheet form, said cathode being an annealed, surface hard-

ened, cold rolled and surface polished alloy in sheet form having the composition; chromium 17 to 19 per cent, nickel 11 to 13 per cent, molybdenum 2 to 4 per cent, and the balance iron, removing the cathode and its attached deposit from the electrolyte, washing it with water and drying it, flexing the cathode and removing the metallic deposit therefrom, removing traces of adhering metallic deposit from said cathode, washing the cathode with water, removing dirt and grease from the cathode, and imparting a polish to the surface of the cathode.

5. A process for the electrolytic deposition of

manganese on a cathode and removing it therefrom which comprises passing a direct current between an anode and a cathode and through an electrolyte containing a manganese salt in solution therein, the cathode being in sheet form and having the composition; chromium about 17 to about 19 per cent, nickel about 11 to about 13 per cent, molybdenum about 2 to about 4 per cent and the balance iron, plating metallic manganese on said cathode and stripping from said cathode the manganese plated thereon.

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