

[54] **ELECTRODEPOSITION OF THICK NICKEL DEPOSITS ON PERMANENT CATHODE BLANKS**

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[58] Field of Search 204/112, 281, 12

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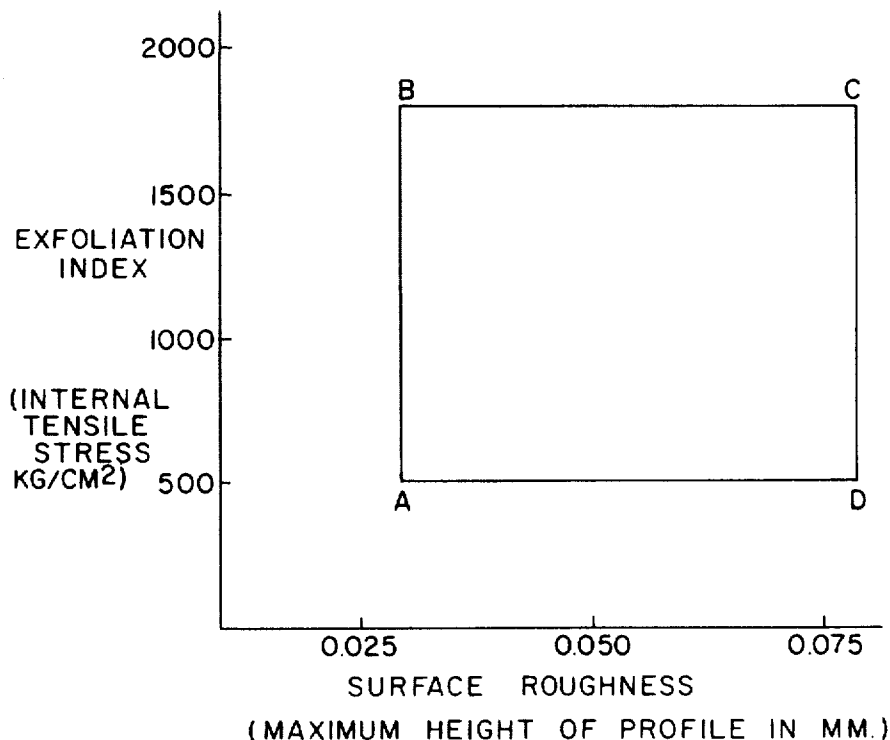
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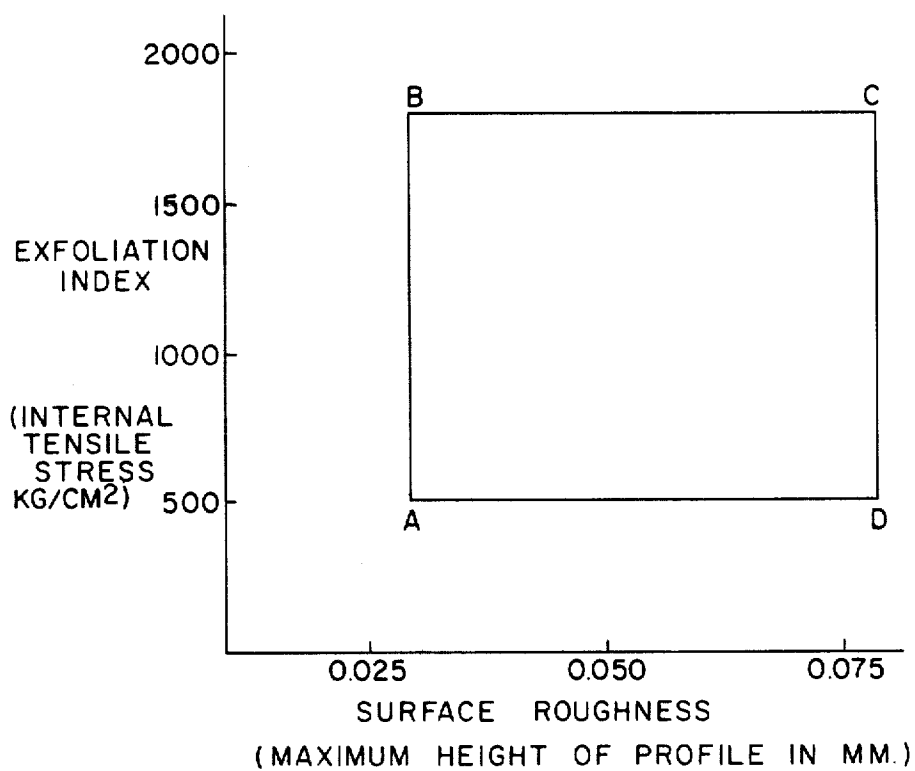
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[57] **ABSTRACT**

A process for electrodepositing nickel deposits of area at least one square decimeter and at least one millimeter thick wherein forces promoting exfoliation of the deposit are balanced against surface roughness of a permanent cathode blank so as to insure adhesion of the deposit to the cathode blank during deposition and enable easy removal of the deposit from the blank after deposition is completed.

8 Claims, 1 Drawing Figure



ELECTRODEPOSITION OF THICK NICKEL DEPOSITS ON PERMANENT CATHODE BLANKS

The present invention is concerned with electro-winning and electrorefining nickel and more particularly with electrowinning (and electrorefining) nickel from an essentially all-sulfate electrolyte which is characterized by a deposit tensile stress not higher than about 1800 kg/cm² as measured by a Brenner-Senderoff contractometer

In a system for recovery of nickel ores, residues and the like comprising leaching of the ore or residue and electrolytic recovery of the nickel, the leachant is very often an aqueous solution of sulfuric acid. In order to avoid problems, particularly some of the more severe corrosion problems and problems of high tensile stress, it is desirable, in so far as possible, to avoid introducing contaminants such as chloride ion into the system. In addition, because of reasons of product purity it is necessary that the electrolyte from which nickel is recovered by electrodeposition be relatively free from sulfur dioxide, thiosulfate or similar reagents which tend to permit codeposition of sulfur in the electrodeposited nickel and lower internal stress in the electrodeposits,

Another desideratum of a system for nickel recovery as described in the preceding paragraph is that the system be automated as much as possible. In the conventional electrorefining of nickel one area where considerable manual labor is involved is in the preparation of nickel starting sheets. These thin sheets i.e., about 0.3 millimeter (mm) thick, must be electrodeposited on blanks, manually separated from the blanks, sheared and mechanically formed. These operations are tedious and expensive. Thus it is desirable to avoid using starting sheets and use instead, permanent cathode blanks or mandrels made of corrosion resistant materials such as stainless steel, titanium and especially, in view of low cost, aluminum. For such blanks or mandrels (ideally in the form of flat sheets about one meter square) to be practical, they must be capable of multiple reuse with minimal refinishing cost; they must reliably retain essentially sulfur-free electrodeposited nickel of relatively high positive internal stress during electrodeposition over extended areas to thicknesses of at least about one millimeter; they must not introduce high ohmic resistance between the mandrel surface and the nickel electrodeposit and, they must readily and controllably release the thick nickel electrodeposit after electrodeposition is complete through application of automated releasing means. Capability of multiple reuse implies resistance to corrosion in the electrolyte even under conditions where no current is passing.

The multiple factors of a controlled chloride-free electrolyte composition, a low sulfur, thick, cathode nickel deposit and the specific requirements for proper permanent cathode functioning all combine to provide a problem which, prior to the work of applicants, has been solved satisfactorily on an industrial scale.

It is an object of the present invention to provide a practical process for electrodepositing essentially sulfur-free nickel on full size (about one meter square) permanent cathode mandrels from an essentially all sulfate, nickel electrolyte.

Other objects and advantages will become apparent from the following description taken in conjunction with the drawing which is a graph interrelating Exfolia-

tion Index (as hereinafter defined) and cathode mandrel roughness.

Generally speaking, the present invention contemplates a process for electrolytically recovering nickel comprising electrodepositing nickel to a thickness of at least about one millimeter from an aqueous sulfate electrolyte substantially devoid of chloride ion over at least about 1 square decimeter (dm²) of uninterrupted area on each side of an edge masked, planar, sheet metal cathode blank made of a metal resistant to corrosion by aqueous sulfuric acid under conditions such that surface roughness of the sheet metal cathode blank produced by abrasive blasting is correlated, as set forth hereinafter, to the internal stress of the electrodeposit (within the range of (+) 500 to 1800 kilograms per square centimeter) to the maximum dimension of the uninterrupted area of the deposit and to the thickness of the electrodeposit so that adhesion to the mandrel will be maintained during electrodeposition and so that the finished deposit can be readily removed from the mandrel by automatic means.

The aqueous, chloride free electrolyte from which the nickel is deposited usually contains about 40 to about 110 grams per liter of nickel (g/l), introduced essentially, as the sulfate, about 100 to about 200 g/l of sulfate ion, and about 5 to about 50 g/l of boric acid. The electrolyte can also contain amounts of essentially inert, current-carrying cation such as sodium and magnesium up to about 100 g/l to decrease the ohmic resistance of the electrolyte. The pH of the pregnant electrolyte is usually controlled within the range of about 1.5 to about 5.5. In carrying out electrowinning from this electrolyte it is usual to take a bite of about 5 to 30 grams per liter of nickel measured as the difference in nickel concentration between input or pregnant electrolyte to a cell and electrolyte exiting from the cell. The temperature in the electrowinning cell is maintained at about 50°C. to about 95°C. and an insoluble anode electrode, (e.g., ruthenium-oxide-coated titanium or lead alloy) is used as an anode. The cathode current density is maintained in the range of about 1.5 to about 10 amperes per square decimeter (a/dm²).

Cathode blanks employed in the process of the present invention are made of metal resistant to attack in mildly acidic sulfate solutions. Advantageously the cathode blanks are made of chromium-containing iron base alloy, i.e., stainless steel or titanium or aluminum (including alloys rich in titanium and aluminum which behave electrochemically in a manner similar to titanium or aluminum). On a full commercial scale, each individual cathode blank is a sheet about one millimeter thick and about one meter square. The edges of the cathode blank are masked, for example, with polyethylene shields or otherwise configured so as to prevent metal deposition at the edges and envelopment of the cathode blank by the deposited metal. The cathode blanks are placed in cells opposite anodes so that metal is deposited on both sides of the blank simultaneously to equalize stresses on the blank. As is usual in nickel electrorefining, cathode blanks may be bagged, with purified electrolyte introduced into the cathode compartment enveloped by the bag to maintain a hydrostatic head on the catholyte. A sparging gas stream, as set forth and described in copending Canadian patent application No. 163,360 can be used in the catholyte compartment to agitate the catholyte and enable the

use of cathode current densities on the high side while maintaining excellent quality of the cathode deposit.

Cathode blanks used in the process of the present invention are prepared for use by abrasive blasting the sheet surface (usually an as-received rolled surface) to a roughness having a maximum height of profile within the range of about 0.030 to about 0.075 millimeters (a metric conversion of maximum surface profile measurement in thousands of an inch as described in Surface Preparation Specifications, Commercial Blast Cleaning Number 6, SSPC-SP6-63, Oct. 1, 1963. The maximum height of profile is the height of standard anchor pattern produced on the surface measuring from the bottoms of the lowest pits to the tops of the highest peaks).

The maximum height of profile produced by a number of different abrasives has been reported in this specification as follows:

Abrasive	Maximum Particle Size (US Sieve Series)	Maximum Height of Profile
Sand, very fine	through 80 mesh	0.038 mm
Sand, fine	through 40 mesh	0.048 mm
Sand, medium	through 18 mesh	0.064 mm
Sand, large	through 12 mesh	0.071 mm

Surface roughness in the required range can be obtained by sandblasting with No. 1 or 2 grade sand having an average particle size in excess of 30 mesh using a cabinet type sand blast device. Those skilled in the sand blasting art will appreciate that exact conditions of sandblasting will vary depending upon differing hardness of the metal of the blank, exact sand grade and sizing, changes in the average velocity and angle of the sand impinging on the metal and the like. Those skilled in the sand-blasting art will also appreciate that other abrasive grits can be employed e.g., microspheres of glass, aluminum oxide and the like. Metallic grit such as iron shot or grit should be avoided in as much as metallic contamination on the cathode blank surface can cause changes in electrochemical behavior of the aluminum, titanium or stainless steel and cause contamination of the electrodeposited nickel.

The degree of roughness of the cathode blank determines to a significant extent the ability of the blank to adhere to or grab onto electrodeposited metal. The greater the roughness of the blank, the greater is the adherence of the metal to the blank. Counteracting the adhesion generated by the roughness of the blank and the inherent adhesion of electrodeposited metal to a given substrate is the internal stress in the electrodeposited metal acting over a distance from a point or line of neutral stress. When nickel is deposited on a planar surface, positive internal stress causes compression forces which are balanced at the center of the planar surface. This stress distribution causes exfoliation of the electrodeposit starting from the perimeter of the electrodeposit and results in a dishing of the exfoliated sheet. The wider the expanse of the planar surface, the greater the forces causing exfoliation at the perimeter. Also the thicker the electrodeposit, the greater the forces causing exfoliation. The factors or conditions of deposit thickness, lateral extent and internal stress are interrelated for purposes of the present invention by the following relationship designated "Exfoliation Index"

$$[f(T) \times f(W)] \times A(S) = E.I.$$

where T is thickness in centimeters, W is width or length (whichever is greater) in centimeters, A is a constant, S is stress in kilograms per square centimeter and $E.I.$ is the Exfoliation Index.

Since the present invention is concerned primarily with depositing full size cathode deposits of area approximately one square meter (per side), the general form of the Exfoliation Index can be normalized. For a deposit of this area and thickness 1-6 millimeters the factor $f(T) = f(w)$ can be considered unity so that the normalized $E.I.$ equals the deposit tensile stress. Again for deposits of this area and thickness, the $E.I.$ can be related to the surface roughness as set forth in the drawing. Electrodeposition is carried out in accordance with the present invention under conditions plottable within the line ABCDA of the drawing.

Deposition conditions plottable above line BC result in the deposit exfoliation in the bath, dropping off the cathode or causing short circuits with the anode or tearing of the cathode bag. Under conditions plottable below line AD the electrodeposit adheres to the cathode so strongly that it is difficult to remove after deposition is complete. Under conditions plottable to the left of line AB, deposit to cathode plate adhesion is unreliable or very low internal stress in the deposit is required which very low internal stress is unobtainable in sulfur-free nickel deposits. Conditions plottable to the right of line CD are difficult to obtain in a controlled manner by sandblasting or other high speed, cheap roughening technique.

It is to be noted that the drawing refers only to full size deposits of thickness 1-6 mm. Exfoliation is affected by the thickness and width or length of the deposit in addition to the tensile stress in accordance with the formula presented to define $E.I.$ Deposits of thickness less than 1 mm. are difficult to strip automatically. Therefore, when considering deposits of smaller area than one square meter the restriction imposed by area ABCDA can be somewhat relaxed. For example, with one square decimeter deposits, a slightly smoother sandblasted surface could be used. For each size of area of deposit the envelope ABCDA must be determined empirically.

In full scale electrowinning of nickel using cathode plates about 1 meter square and depositing to a thickness of about 0.6 cm, the control of the Exfoliation Index resolves itself into controlling the internal stress of the sulfur-free (i.e., up to only about 0.004% sulfur) nickel deposit within the range of about 500 to about 1800 kilograms per square centimeter (kg/cm^2). Basically, that is done by electrodepositing from the electrolyte free from chloride ion and sulfur containing additives and under the conditions as set forth hereinbefore observing generally that as the temperature increases within the range the tensile stress decreases (e.g., 40°C tensile stress 1800 kg/cm^2 ; 70°C, 1100 kg/cm^2 and 85°C, ~700 kg/cm^2 , all measurements at pH 3.0), and as the pH increases within the range the internal tensile stress increases slightly.

Particularly attractive conditions of low tensile stress for electrodeposition of thick nickel deposits onto reusable cathode blanks are achieved by the use of the following conditions:

40 to 120 g/l Ni, 0 to 50 g/l H_3BO_3 and 0 to 75 g/l Na_2SO_4 temperature of 85° to 95°C for which the resulting

tensile stresses are about 700 kg/cm². A bag free nickel electrowinning cell, based on the above conditions, and designed to operate with a nickel bite of 7-15 g/l, a current efficiency of about 75% and a current density of 2 to 10 amp/dm² has been described in a disclosure by the present inventors along with B. Tilak.

In order to give those skilled in the art a better understanding and appreciation of the invention the following examples are given:

EXAMPLE I

Thick nickel deposits, 170 ampere hours per square decimeter (amp-hr/dm²) (~2 mm) were deposited by electrowinning nickel in conventional bagged cathode cell from pregnant electrolyte containing 65 g/l Ni, 150 g/l Na₂SO₄, and 10 g/l H₃BO₃ and having a pH of 30 at 65°C, at a current density of 4 amp/dm² at a current efficiency 90% and at a nickel bite of 15 g/l. Edge masked titanium cathode blanks of surface area 1 dm² (per side) were prepared by sandblasting with number one sand with no additional treatment. No exfoliation was observed when the run was terminated due to electrolyte depletion. Tension stress in nickel electrodeposited from this electrolyte was about 1050 kg/cm².

EXAMPLE II

About 220 amp-hr/dm² (~3 mm) thick nickel was deposited by electrowinning in a conventional bagged cathode cell from pregnant electrolyte containing 65 g/l Ni, 10 g/l Mg and 10 g/l H₃BO₃ and having a pH of 3.0 at 60°C, at a current density 2 amp/dm², at a current efficiency 90%, and at a bite of 15 g/l Ni. An edge masked titanium cathode blank of surface area 1 m² (per side) was prepared by sandblasting with number two sand with no further treatment. Again no exfoliation was observed when the run was terminated due to electrolyte depletion. Tensile stress in Ni electrodeposited from the electrolyte was 1050 kg/cm².

EXAMPLE III

About 390 amp-hr/dm² (~5mm) thick nickel was deposited by electrowinning in a conventional bagged cathode cell from pregnant electrolyte containing 80 g/l Ni, 10 g/l Mg and 10 g/l H₃BO₃ and having a pH of 3.0 at 60°C, at a current density 8 amp/dm², at a current efficiency 80% and at a bite of 30 g/l Ni. An edge masked aluminum cathode blank of area 1 dm² was prepared by sandblasting. Again no exfoliation was observed when the run was terminated, and the deposit was readily removed from the blank. Tensile stress in nickel deposited from this electrolyte was about 980 kg/cm².

EXAMPLE IV

About 150 amp-hr/dm² (~2 mm) thick nickel was deposited by electrowinning in a bagged cathode cell from pregnant electrolyte containing 60 g/l Ni, 150 g/l Na₂SO₄ and 16 g/l H₃BO₃ and having a pH of 3.0 at 55°C, at a current density 2 amp/dm², at a current efficiency 82% and at a bite of 12 g/l Ni. The cathode consisted of edge masked stainless steel (AB finish) of area 1 dm² (each side). No evidence of deposit exfoliation was observed. Tensile stress in nickel deposited from this electrolyte was about 1050 kg/cm².

EXAMPLE V

About 200 amp-hr/dm² (~2.5 mm) thick nickel was

deposited by electrowinning in a conventional bagged cathode cell from pregnant electrolyte containing 80 g/l Ni, 10 g/l Mg and 10 g/l H₃BO₃ and having a pH of 2.9 at 60°C, at a current density of 3 amp/dm², at a current efficiency of 80% and a bite of 25 g/l Ni. An edge masked aluminum cathode blank of area 1 m² was prepared by sandblasting with number two grade sand. Again no exfoliation was observed when the run was terminated, and the deposited was readily removed from the blank.

EXAMPLE VI

About 2.4 mm nickel deposit was deposited by electrowinning in a conventionally bagged cathode cell from pregnant electrolyte containing 72 g/l Ni, 5 g/l MgSO₄, 44 g/l H₃BO₃ and 75 g/l Na₂SO₄ having a pH of 5.5 at a current density of 10 amp/dm², a current efficiency of 77% and a bite of 12 g/l Ni at a cell operating temperature of 85°C. An edge masked titanium cathode blank of area 1 dm² was prepared by sandblasting with number one grade sand. The tensile stress in the electrodeposited nickel was 700 kg/cm². Again no exfoliation was observed when the run was terminated, and the deposit was readily removed from the blank.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for electro-deposition of nickel comprising electrodepositing substantially sulfur-free nickel continuous over an area of at least about 1 square decimeter to a thickness of at least about 1 millimeter on an abrasively roughened, permanent mandrel made of titanium, aluminum or stainless steel from an aqueous sulfate bath substantially devoid of chloride and having a pH in the range of about 1.5 to about 5.5 under conditions whereby the Exfoliation Index of the deposit is correlated to the surface roughness of the mandrel so as to provide adhesion during electrodeposition and ready removal of the deposit from the mandrel upon completion of the electrodeposition.

2. A process for electrodeposition of nickel comprising electrodepositing substantially sulfur-free nickel continuous over an area of about 1 square meter to a thickness of at least about one mm. on an abrasively roughened permanent mandrel made of titanium, aluminum or stainless steel from an aqueous sulfate bath substantially devoid of chloride and having a pH in the range of about 1.5 to about 5.5 under conditions so that the Exfoliation Index of deposition plotted against the surface roughness of the mandrel is representable by a point lying within the area A,B,C,D,A on the accompanying drawing.

3. A process as in claim 2 wherein the sulfur-free nickel has a positive internal stress of about 500 to about 1800 kilograms per square centimeter.

4. A process as in claim 1 wherein the sulfur-free nickel has a positive internal stress of about 500 to 1800 kilograms per square centimeter.

5. The process of claim 2 wherein the electrodeposition occurs during electrowinning of nickel.

6. The process of claim 2 wherein the mandrel is made of stainless steel.

7. The process of claim 2 wherein the mandrel is made of titanium.

8. The process of claim 2 wherein the mandrel is made of aluminum.

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