⑲ **Europäisches Patentamt**
European Patent Office
Office européen des brevets

⑪ Publication number: **0 006 759**
A1

⑫
EUROPEAN PATENT APPLICATION

㉑ Application number: **79301254.3**

㉒ Date of filing: **28.06.79**

(51) Int. Cl.^{3}: **C 25 D 17/10**

㉚ Priority: **29.06.78 US 920383**

㊸ Date of publication of application: **09.01.80**
Bulletin 80/1

(84) Designated Contracting States: **DE FR GB IT**

(71) Applicant: **INCO EUROPE LIMITED, Thames House Millbank, London SWIP 40F (GB)**

(72) Inventor: **Dill, Aloys John, 32 Drewry Lane, Tappan, New York 10983 (US)**

(74) Representative: **Greenstreet, Cyril Henry et al, Thames House Millbank, London SW1P 4QF (GB)**

(54) Anode materials for use in electrodeposition.

(57) A composite, soluble anode material for use in the electrodeposition of nickel-iron alloys comprising a sheet of iron or low alloy steel coated on both sides with nickel which preferably contains an activator, the ratio of the exposed area of nickel to the exposed area of iron being from 3 to 80.

EP 0 006 759 A1

Anode Materials for use in Electrodeposition

This invention relates to anodes for use in electrodeposition and more particularly to composite anode materials for use in the electrodeposition of nickel-iron alloys.

Electrodeposition of nickel-iron alloys is carried out commercially both for decorative purposes and for the manufacture of magnetizable components for use in the electronics industry. The means by which such electrodeposition can be performed are well known. Consumable anode materials which have been used commercially are of two types, firstly alloy anode materials and secondly individual iron and nickel anode materials in the form of small pieces, ie rounds, squares, pellets, etc, of nickel and iron contained in separate baskets, for example those made of titanium, or in the form of separate nickel and iron slabs. Both types of anode materials previously used suffer from some disadvantages. The principal disadvantages of the separate iron and nickel anodes are firstly the necessity for maintaining separate inventories of iron and nickel, secondly the need in some instances for separate anode controls, thirdly the danger of placing the wrong material in a basket and fourthly the possible effect of the imbalance to the electroplating system if one anode loses current. Alloy anodes have the disadvantage that they must be specially melted and cast and thus are more costly than the basic metals.

It has now been found that such disadvantages can in general be avoided by use of the composite anode material of the present invention.

According to the invention, a composite anode material for use in the electrodeposition of nickel-iron alloys is characterized by the fact that it comprises a sheet of iron or low alloy steel coated on both sides with nickel, the ratio of the exposed area of nickel to the exposed area of iron being from 3 to 80.

The anode material is preferably of suitable size for use in conjunction with an anode basket and therefore, can conveniently be square in shape and have sides measuring from 1 to 10cm. Such square or other suitably shaped pieces of anode material are usefully prepared from a large sheet of composite material of, for example, 1m square which is cut or sheared to provide pieces of the desired shape.

The anode material is preferably prepared by electrodepositing the nickel coating onto the iron or steel sheet although other methods of forming the coating may be employed. For example, a sheet of nickel can be hot rolled onto the iron or steel sheet or alternatively nickel in the form of a powder can be sintered and compacted onto the surface of the iron sheet. Whichever method is employed, it is essential that there is a relatively strong bond between the iron sheet and the nickel coating to avoid possible delamination during shearing or during use of the anode material.

The nickel coating of the anode material can usefully contain, and preferably does contain, an activator for controlling or increasing the dissolution characteristics of the nickel during use of the anode material. Sulphur is an activator which can readily be incorporated into the nickel, particularly when the nickel coating is prepared by electrodeposition onto the iron sheet. A range of up to 5% sulphur can be present in the nickel, suitably up to 0.2% sulphur. Generally, when the sulphur content of the nickel is at the lower end of this range the ratio of exposed area of nickel to exposed area of iron is at the higher end of its range whereas when the sulphur content is high, the ratio of exposed areas is low.

Although sulphur is the preferred activator when the nickel coating of the anode material is produced by electrodeposition, it will be apreciated that other activators may be employed, especially when the nickel coating is prepared by means other than electrodeposition. Examples of such other activating materials include silicon, oxygen and carbon. It is well known that in general the relative activity of nickel under electrocorroding conditions can be controlled by the amounts and type of activator employed.

Consequently, when a particular activator is present in the nickel coating, it is evident that the activator content relative to the ratio of exposed area of nickel to exposed area of iron can be adjusted in a manner similar to that disclosed above with respect to sulphur as an activator.

The sheet bearing the nickel coating can be either iron or a low alloy steel. It will be appreciated that what is desired for the iron portion of the anode material of the invention is a relatively pure iron material. Steels which contain large amounts of elements other than iron, for example, stainless steels are not useful. Likewise, high alloyed carbon steels containing elements such as molybdenum, chromium, tungsten, etc should not be used because of the possibility that these elements will be carried into the electroplating bath and cause contamination. Steels suitable for use in manufacturing the anode material of the present invention include, but are not limited to, the following grades: 1010, 1020 and low carbon grade steels.

The weight ratio of nickel to iron (or steel) can be varied to suit a particular nickel-iron alloy plating bath. Commercial decorative nickel-iron alloy plating baths currently used normally utilise anode materials containing about 15 to about 50% iron when considered as a whole. For example, as a practical matter, an anode containing about 25% iron is suitable for use in most decorative nickel-iron alloy plating baths. However, there is no specific limitation on the weight ratio of the anode material that must be observed.

A prefered method of making the anode material of the invention is to employ a piece of sheet iron or steel of appropriate dimensions, for example, 1m square and about 0.08cm thick as mandrel on which sulphur-containing nickel is electrodeposited during a typical nickel electrowinning or electrorefining operation. It is convenient to deposit approximately 0.32cm of nickel containing about 200 to 300 parts per million (ppm) of sulphur on both sides of the iron mandrel. Following completion of electrodeposition of the sulphur-bearing nickel, the plated mandrel is removed from the electrolytic cell washed, dried, and sheared into appropriate sized pieces such as squares or rectangular pieces. Alternatively, the iron mandrel bearing the electro deposited nickel can be "blanked" to form round or oval pieces and the scrap sheared to produce irregular pieces of anode material. It will also be appreciated that the cathode mandrel, eg the iron sheet in an electrowinning operation, can be selectively masked to provide lines of weakness where the mandrel can be sheared with less effort than required with an unmasked mandrel. In general however, such masking is unnecessary and is somewhat troublesome in that it dictates the size of the end product at a time when the size required may not be readily determinable.

The nickel-iron anode material can be typically employed in a commercial nickel-iron aqueous sulphate electrolyte containing about 30 to 120 g/l of nickel, about 1 to about 10 g/l of iron, about 10 to about 75 g/l of chloride ion, about 30 g/l to about saturation with boric acid, a bath stabilizer to prevent precipitation of iron hydrate (iron hydroxide) and a stress reducer with the balance being water. The pH of the electrolyte is maintained at about 2.3 to about 4.2. In this bath, a stabilizer can be either a reducing agent such as ascorbic acid or an isomer of ascorbic acid to maintain iron in the ferrous state or it can comprise a complexing agent such as sodium gluconate or sodium oxalate which will complex ferric ions in solution. A typical stress reducer used along with a bath stabilizer in commercial baths is sodium saccharin. This bath can be operated at temperatures of about 50 to about 75°C and adjustments of bath composition can be performed as necessary. The anode material of the invention can be employed in this bath at an anode current density of about 1.0 to about 7.5 A/dm^2. Other types of nickel-iron baths can be employed with other electroplating conditions usual to those baths.

Some examples will now be given.

EXAMPLE Ia

Anode material in accordance with the invention was prepared by electrodepositing 0.119cm of nickel containing about 200 to 300 ppm sulphur on both sides of a 0.079cm thick iron sheet. The sheet was then sheared into square pieces having 2.54cm edges to form anode material of the invention having a ratio of exposed area of nickel to exposed area of iron of about 19. The material of this example contained about 75% nickel, 25% iron.

EXAMPLE Ib

Anode material was made in the same way as in Example Ia except that type 1010 steel sheet 0.094cm thick was used instead of iron sheet and the nickel was electrodeposited to a thickness of 0.131cm to produce a ration of surface area of nickel to exposed area of iron of about 16.3. The material of this example also contained about 75% nickel, 25% iron.

EXAMPLE Ic

Anode material was made in the same way as in Example Ia except that the nickel was essentially free of an activator, containing only 5 to 10 ppm sulphur.

EXAMPLE Id

Anode material was made in a similar manner to Example Ib except that the nickel was electrodeposited to a thickness of 0.093cm to produce anode material containing about 65% nickel, 35% iron. The ratio of exposed nickel to iron surface area of the anode material of this example was about 15.5.

EXAMPLE Ie

Anode material is made in the same way as Example Ib except for the fact that the sheet was sheared into square pieces having edges of 1.27 cm to form anode material having a ratio of surface area of nickel to exposed area of iron of about 11.0.

EXAMPLE II

The anode material of Examples Ia and Ib were electro-dissolved separately in a titanium basket in a plating bath having the following nominal composition at the start of dissolution:

$NiSO_4.6H_2O$	300 g/l
$NiCl_2.6H_2O$	60 g/l
H_3BO_3	30 g/l
Sodium Gluconate	20 g/l
Sodium Saccharin	0.2 g/l

The bath was operated at a temperature of 60°C and pH was maintained at about 3.2. The superficial anode current density was 2.7 A/dm^2 and the cathode current density was 2.7 A/dm^2. Over a period of 32 and 44 days the anode materials of Example Ia and Ib respectively dissolved and after an initial equilibration period established the equilibrium composition of the electrolyte with respect to ionic nickel/iron ratio and maintain this composition substantially constant. The cathodic depositsproduced were of commercial quality.

EXAMPLE IIIa

The anode material of Example Ia was electro-dissolved in a titanium basket in a proprietary decorative nickel-iron alloy plating bath having the following nominal composition at the start dissolution as recommended by by the bath manufacturers:

$NiSO_4.6H_2O$	105 g/l
$NiCl_2.6H_2O$	60 g/l
H_3BO_3	45 g/l
Total Iron	2 g/l

plus proprietary additives as recommended the bath manufacturer.

The bath was operated at a temperature of 60°C and pH was maintained in the range of 2.8 to 3.5. Brightener additions were made as recommended during plating.

The superficial anode current density was 3.6 A/dm^2 and the cathode current density was 5.4 A/dm^2. Over a period of 42 days the anode material of Example Ia dissolved and after an initial equilibration period established and maintained the equilibrium composition of the electrolyte as in Example II. The cathodic deposit was bright and level and of decorative quality.

EXAMPLE IIIb

The anode material of Example Id was electro-dissolved in a titanium basket in a proprietary decorative nickel-iron alloy plated bath which was different to that of the previous Example. This bath had the following nominal composition at the start of dissolution as recommended by the bath manufacturer:

$NiSO_4.6H_2O$	85 g/l
$NiCl_2.6H_2O$	135 g/l
H_3BO_3	45 g/l

proprietary additive as recommended by the bath manufacturer.

The bath was operated at a temperature of 57°C and the pH was maintained in the range of 3.5 to 4.0. Brightener additions were made as recommended during plating. Anode and cathode current densities were the same as in Example IIIa. Over a period of 30 days the anode material of Example Ib dissolved and after an initial equilibration period established and maintained the equilibrium composition of the electrolyte as in Example II. The cathodic deposit was bright and level and of decorative quality.

EXAMPLE IIIc

The anode material of Example Ie was electro-dissolved as in Example IIIb in a third proprietary decorative nickel-iron alloy plating bath. This bath had the following nominal composition at the start of the dissolution as recommended by the bath manufacturer:

$NiSO_4.6H_2O$	120 g/l
$NiCl_2.6H_2O$	90 g/l
H_3BO_3	43 g/l

proprietary additive as recommended by the bath manufacturer.

The bath was operated at a temperature of 57°C and the pH was maintained in the range of 3.4 to 4.2. Brightener additions were made as recommended during plating. Anode and cathode current densities were the same as in Example IIIb. Over a period of 31 days the anode material of Example Ie dissolved and after an initial equilibration period established and maintained the equilibrium composition of the electrolyte as in Example II. The cathode deposit was bright and level and of decorative quality.

EXAMPLE IV

The anode material of Example Ic was electrodissolved in a titanium basket in the plating bath of Example II and under the same operating conditions as Example II. Over a period of 39 days the anode material of Example Ic dissolved and after an initial equilibration period established the equilibrium composition of the electrolyte with respect to ionic nickel/iron ratio and maintained this composition substantially constant. The cathodic deposit was of commercial quality.

The equilibrium composition of this electrolyte was however not maintained constant using the anode of Example Ic as was the equilibrium composition of the electrolyte in Example II which used the anodes of Example Ia or Ib. Abrupt changes in iron content relative to nickel about the equilibrium composition occurred as the anode material of Example Ic dissolved and settled in the anode basket and as fresh anode material was added to the basket. This behaviour indicates an excessive rate of iron dissolution relative to nickel dissolution in the anode material of Example Ic. The fluctuation of iron content of the electrolyte relative to nickel content in this Example was not so great as to render the anode material of Example Ic inoperative because the high ratio of exposed nickel to iron surface area permitted the anode material of Example Ic to function adequately in this Example despite the fact that the nickel contained essentially no activator.

Examples Ia, b, d, e, II and IIIa, b, c, demonstrate a preferred aspect of the anode material of the invention when the nickel portion of the anode contains sulphur as an activator. Examples Ic and IV show the action of anode material of the invention when the nickel is essentially sulphur-free. These Examples taken together demonstrate the importance of correlating the ratio of exposed nickel to iron surface area to the amount of activator in the nickel.

Claims

1. A composite anode material for use in the electrodeposition of nickel-iron alloy, characterised in that it comprises a sheet of iron or low alloy steel coated on both sides with nickel, the ratio of the exposed area of nickel to the exposed area of iron being from 3 to 80.

2. An anode material according to claim 1 characterised in that the iron sheet is coated with the nickel by electrodeposition.

3. An anode material according to claim 1 or claim 2 characterised in that the nickel contains an activator.

4. An anode material according to claim 3 characterised in that the activator is sulphur in a range of up to 5% of the nickel.

5. An anode material according to claim 4 characterised in that the sulphur is present in the nickel in an amount up to 0.2%

6. An anode material according to claim 4 or claim 5 characterised in that when the sulphur is at the lower end of the range, the ratio of the exposed area of nickel to the exposed area of iron is at the higher end of the range and when the sulphur is at the higher end of its range, the ratio of the exposed area of nickel to the exposed area of iron is at the lower end of its range.

7. An anode material according to any preceding claim characterised in that it comprises a plurality of relatively small pieces cut or sheared from a larger size sheet.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 79 30 1254

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	FR - A - 954 096 (STANDARD STEEL SPRING CO.) * Pag3 , line 72 * --	
A	GB - A - 520 212 (DEUTSCH AND BRENNER LTD.) --	
A	GB - A - 520 211 (DEUTSCH AND BRENNER LTD.) --	
A	DE - B - 1 259 666 (IBM) * Column 6, lines 15-16 * --	
A	GB - A - 539 882 (THE MOND NICKEL CO.) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 25 D 17/10

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 25 D 17/10

CATEGORY OF CITED DOCUMENTS

- 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

☑ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	02-10-1979	NGUYEN THE NGHIEP

EPO Form 1503.1 06.78