GOVERNMENT OF INDIA, THE PATENT OFFICE, 214, Acharya Jagadish Bose Road, Calcutta-17. Complete specification No. 148078 dated 11th August 1978. Application and provisional specification No. 160/Del/77 dated 16th July 1977. Acceptance of the complete specification advertised on 11th October 1980.

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" PROCESS FOR THE PRODUCTION OF ELECTROFORMED COPPER FOIL "

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi -1, India, an Indian Registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification describes the nature of this invention.

This is an invention by Balkunje Anantha Shenoi, Scientist; Sandip Kumar Roy, Scientist ; Venkataraman Sivan, Scientist and Subbiah John, Senior Technical Assistant, all of them are employed in the Central Electrochemical Research Institute, Karaikudi 6 and all are indian national.

Price Rs.2.00

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This invention relates to chemical pretreatment of titanium mandrels.

Hitherto it has been proposed to use titanium or other mandrels for the production of copper foils.

The drawbacks of other mandrels lie in the fact that they fail to give

i) a pore free foil and ii) a smooth scratch free surface.

Though titanium overcomes the latter shortcoming it has an oxide film which leads to the following additional difficulties.

i) Detachment of copper foil from the mandrel during electroforming

ii) Formation of foils with dull mandrel facing surface

iii) Formation of pores in the copper foil.

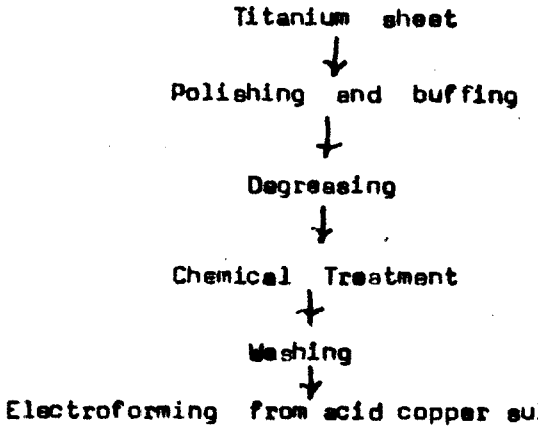
The object of the present invention is to obviate the above difficulties encountered in electroforming with an untreated titanium mandrel by suitable chemical pretreatment of the surface.

To this end the invention broadly consists in applying a chemical treatment(2-20 minutes) to a polished titanium mandrel with one of the following solutions:

1. Hydrofluoric acid - Sp.gr. 1.13 (5 to 10% by volume) Nitric acid- Sp.Gr. 1.41 - 1.42 (5 to 10% by volume).
2. Hydrofluoric acid - sp.gr. 1.13 (10 to 20% by volume) Nitric acid - Sp.gr. 1.41 (30-60% by volume) Sodium dichromate (2 to 3% by weight)
3. Hydrofluoric acid (2-10%) by volume). Chromium trioxide (2 to 20% by weight)
4. Hydrochloric acid (3-15% by volume) - Sp.gr. 1.18 and Hydrofluoric acid (5 to 10% by volume).
5. Hydrochloric acid - Sp.gr. 1.18 (3-15% by volume) Hydrochloric acid - (5-10% by volume) and Ferric chloride (5 to 10% by weight).

The copper foils obtained after such treatments were found to be shining smooth and pore free.

The following is the flow chart for the process:



The following are the examples to illustrate the process and not to limit the scope of the invention:

Example 1

Titanium sheet of size 6" x 6" was polished and buffed in the usual manner till a scratch free surface was obtained. The titanium mandrel is then degreased with trichloroethylene. The titanium cathode was treated with a solution containing 5% HF, 10% HNO_3 and rest water, for 5 minutes at room temperature. The cathode was washed thoroughly with distilled water. Electroforming of copper was then carried out from an acid copper sulphate bath for a predetermined time. The foil is then peeled off, washed and dried. It is found to be smooth, lustrous and pore free.

Example 2

Titanium sheet of size 6" x 6" after the usual polishing, buffing and cleaning operations was treated with a solution containing 10% HF, 30% HNO_3 3% by weight $Na_2Cr_2O_7$ and rest water for 10 minutes at room temperature. The treated mandrel was thoroughly washed with distilled water and electroforming was then carried out from an acid copper sulphate bath for a predetermined time. The foil was then detached from the mandrel, washed and then dried. The mandrel facing side of the foil is found to be smooth shining and pore free.

Example 3

Titanium sheet of size 6" x 6" after polishing, buffing and cleaning as indicated in the above examples was treated with a solution of 10% HF, 20% by weight CrO_3 and rest water for 2 minutes at room temperature. The mandrel was then washed thoroughly with distilled water and transferred to an acid sulphate electroforming bath. Electroforming was carried out for a ~~max~~ predetermined time. The foil was then removed from the mandrel, washed thoroughly and dried. The mandrel facing surface of the foil was found to be lustrous, smooth and pore free.

Example 4

Titanium sheet of size 6" x 6" after the usual polishing, buffing and cleaning operations was treated with a solution containing 15% HCl, 10% HF and rest water for ten minutes at room temperature. The mandrel was then washed thoroughly with distilled water and transferred to an acid sulphate bath. Electroforming was carried out for a known time. The foil was then removed from the mandrel, washed and dried. The mandrel facing side of the foil was found to be lustrous, smooth and pore free.

Example 5

Titanium sheet of size 6" x 6" after the usual polishing, buffing and cleaning was treated with a solution containing 10% HCl, 5% HF and 10% by weight $FeCl_3$ and rest water for 20 minutes at room temperature. The mandrel was then washed thoroughly with distilled water and transferred to the tank containing acid sulphate bath. Electroforming was carried out for a fixed time. The foil was then peeled off from the mandrel, washed and dried. The mandrel facing side of the foil was found to be lustrous smooth and pore free.

The following are the main advantages of the above inventions

1. The electroformed copper foil is pore free.
2. The side facing the mandrel is found to be lustrous, smooth and shining
3. The peeling of the foil from the mandrel is made easy
4. The chemicals used for pretreatment are indigenously available.

Dated this 13th day of July, 1977.

I. M. S. MAMAK
Scientist E (Patents)
Council of Scientific & Industrial Research

148078

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

" PROCESS FOR THE PRODUCTION OF ELECTROFORMED COPPER FOIL "

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian Registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

148078

This is an invention by Balkunje Anantha Shenoi, Scientist, Sandip Kumar Roy, Scientist, Venkataraman Sivan, Scientist and Subbiah John, Senior Technical Assistant, all of them are employed in Central Electrochemical Research Institute, Karaikudi-623006 and all are Indian nationals.

This invention relates to a process for the production of electroformed copper foil and the pretreatment of titanium mandrel for the purpose.

The drawbacks in the use of other mandrel lie in the fact that they fail to give

a) a pore free foil
b) a smooth shiny and lustrous surface

Though titanium overcomes the latter shortcoming it has an oxide film which leads to the following additional difficulties.

a) Detachment of copper foil from the mandeal during electro forming
b) Formation of foils with dull finish facing the mandrel surface
c) Formation of pores in the copper foil.

The main object of the present invention is to obviate these disadvantages by using a chemical pretreatment step for the titanium mandrel for the production of electroformed copper foils.

The other main objects of the invention are that :

a) the electroformed copper foil is pore free
b) the side facing the mandrel is lustrous, smooth and shiny
c) the peeling of the foil from the mandrel is made easy, and
d) the chemicals used for pretreatment are indigenously available.

The main finding underlying the present invention consists in the pretreatment of the titanium sheets of the mandrel with aqueous acid solution prior to electroforming of copper foils.

Accordingly the invention provides a process for the preparation of electroformed copper foil by electrolytic deposition of copper on mandrel formed of titanium sheet cathodes in an acid copper bath which is characterised in that the titanium sheet for use as cathode is subjected to a chemical pretreatment in an acidic aqueous solution of hydrofluoric acid and a mineral acid.

According to another feature of the invention the mineral acid used in the acidic aqueous solution may be hydrochloric acid or nitric acid or admixture of both.

Accoring to a further feature of the invention the acid aqueous solution may also contain chromium trioxide, sodium dichromate and ferric chloride alone or an admixture as additives.

According to a still further feature of the invention the acidic aqueous solution may comprise 5 to 10% of V/V of hydrofluoric acid, 0 to 30% of V/V of the mineral acid, 0 to 20% of W/V of sodium dichromate, 0 to 20% of W/V of chromium trioxide and 0-10% of W/V of ferric chloride and the chemical pretreatment of the titanium sheet may be carried at room temperature for 2 to 10 minute.

The invention also further provides that the process may comprise the steps of polishing and buffing, degreasing and chemical pretreatment of the titanium sheet.

The flow chart for this process is shown on the accompanying drawing.

The following typical examples are given to illustrate how the invention is carried out in actual practice but not to limit the scope of this invention.

Example - 1

Titanium sheet of size 15 cm x 15 cm was polished and buffed in the usual manner till a scratch free surface was obtained. The titanium mandrel was then degreased with trichloroethylene. The titanium cathode was treated with a solution containing 5% V/V hydrofluoric acid, 10% V/V nitric acid and

thoroghly with distilled water. Electroforming of copper was then carried out from an acid copper sulphate bath for 10 minutes. The foil was then peeled off washed and dried. It was found to be smooth, shiny, lustrous and pore free.

Example - II

Titanium sheet of size 15 cm x 15 cm after the usual polishing, buffing and cleaning operations was treated with a solution containing 10% V/V hydrofluoric acid, 30% V/V nitric acid, 3% W/V sodium dichromate and rest water for 10 minutes at room temperature. The treated mandrel was thoroghly washed and with distilled water and electroforming was then carried out from an acid copper sulphate bath for 10 minutes. The foil was detached from the mandrel, washed and then dried. The mandrel facing side of the foil was found to be smooth, shining, lustrous and pore free.

Example - III

Titanium sheet of size 15 cm and 15 cm after polishing, buffing and cleaning as indicated in the above examples was treated with a solution containing 10% hydrofluoric acid, 20% W/V CrO_3 and rest water for 2 minutes at room temperature. The mandrel was thoroughly washed with distilled water and transferred to an acid copper electroforming bath. Electroforming was carried out for 10 minutes. The foil was then removed from the mandrel, washed thoroughly and dried. The mandrel facing surface of the foil was found to be lustrous, smooth, shiny and pore free.

Example - IV

Titanium sheet of size 30 cm x 30 cm after the usual polishing buffing and cleaning operations was treated with a solution containing 15% V/V hydrochloric acid, 10% V/V hydrofluoric acid and rest water for ten minutes at room temperature. The mandrel

was then washed thoroughly with distilled water and transferred to an acid sulphate bath. Electroforming was carried out for 15 minutes. The foil was removed from the mandrel, washed and dried. The mandrel facing side of the foil was found to be lustrous, smooth , shiny and pore free.

Example - V

Titanium sheet of size 60 cmx 60cm after the usual polishing, buffing and cleaning was treated with a solution containing 10% V/V hydrochloric acid, 5% V/V hydrofluoric acid, 10% W/V ferric chloride and rest water for 20 minutes at room temperature. The mandrel was then washed thoroughly with distilled water and transferred to the tank containing acid sulphate bath. Electroforming was carried out for 15 minutes. The foil was then peeled off from the mandrel, washed and dried. The mandrel facing side of the foil was found to be lustrous, shiny, smooth and pore free.

We claim:

1. Process for the production of electroformed copper foil by electrolytic deposition of copper on mandrels formed of titanium sheet cathodes in an acid copper bath characterised in that the titanium sheet for use as cathode is subjected to a chemical pretreatment in an acidic aqueous solution of hydrofluoric acid and a mineral acid.

2. Process as claimed in claim 1 wherein the mineral acid used is hydrochloric acid or nitric acid or admixture of both.

3. Process as claimed in claim 1 and 2 wherein the acidic aqueous solution used also contains chromium trioxide, sodium dichromate and ferric chloride alone or in admixture.

4. Process as claimed in any of the preceding claims wherein the acidic aqueous solution comprised 5% to 10% V/V of hydrofluoric acid, 0-30% of V/V of the mineral acid, 0 to 20% W/v of sodium dichromate, 0-20% of W/V of chromium trioxide and 0-10% W/V of ferric chloride and the chemical pretreatment of the titanium sheet

is carried at room temperature for 2 to 15 minutes.

5. Process as claimed in any of the preceding claims 1 to 3 wherein the acidic aqueous solution comprises 5 to 10% V/V of hydrofluoric acid, 5-15% of V/V of hydrochloric acid, 10-30% V/V of nitric acid, 2-20% W/V of chromium trioxide, 3-20% of W/V of sodium dichromate and 5-10% W/V of ferric chloride.

6. Process for the production of electroformed copper foil substantially as herein described and illustrated.

ORIGINAL

Dated this 10th day of August 1978.

(I.M.S.MAMAK)
Scientist, Patents.
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

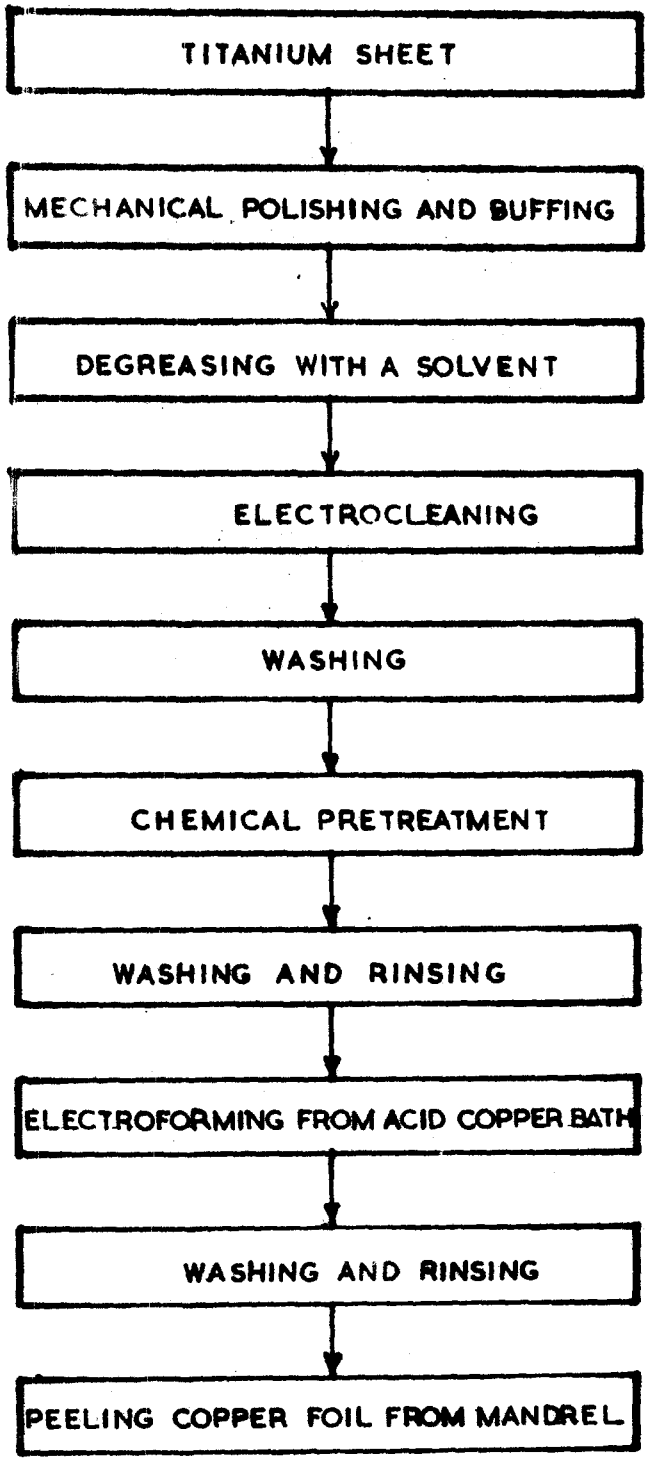
COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

No. 148078.

No. OF SHEETS: 1

SHEET No. : 1



A. KUMAR,
ASST. PATENTS OFFICER,
C.S.I.R.