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PRODUCTION OF COMPOSITE METAL SHEET OR STRIP

Alfred Frank Scutt, Ealing, London, and Alan Arthur Bourne, Harrow, England, assignors to Johnson, Matthey & Company Limited, London, England, a British company

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4 Claims. (Cl. 29—497.5)

This invention relates generally to improvements in the production of composite metal sheet or strip, more particularly in the form of a basis metal of refractory metal, having bonded thereto one or more strips of noble metal forming inlay bi-metal sheet or strip.

The principal object of this invention is to provide an improved method of making composite metal sheet or strip of the above kind.

Another object of the invention is to provide an improved method of making composite noble metal striped-refractory metal electrodes which ensures that a strong and lasting bond is obtained between the noble metal and the refractory metal.

A particular application of the method of the invention lies in the production of composite titanium-platinum electrodes for use in the cathodic protection of ships, plant etc. or in electrochemical processes such as electrolysis.

A limited object of the invention, therefore, is to provide an improved composite titanium-platinum anode which is not subject to the defects of existing anodes of this kind, and an improved method of making such an anode.

For the sake of simplicity in the following description, the invention will be described in relation to the production of electrodes of the above kind, although it is to be clearly understood that no limitation is intended thereby, the invention being equally applicable to the production of electrodes comprising another refractory metal than titanium, such, for example, as tantalum, niobium or zirconium and/or another noble metal than platinum, such, for example, as a platinum base alloy and also to the production of composite sheet or strip for other purposes than as electrodes.

Platinum-clad-titanium anodes for cathodic protection or electrolytic purposes are well-known, and it has recently been established that it is not necessary for the titanium to be covered with a continuous layer of platinum, but that anodes of the same or substantially the same efficiency can be obtained if the platinum be applied in the form of spaced, preferably parallel, strips to form an anode comprising a sheet of titanium striped with platinum.

It has already been proposed to make electrodes of this kind either by electrodepositing the platinum on to the surface of a titanium sheet, or by means of a roll bonding procedure.

In the electrodeposition method, the platinum stripes are obtained by first applying "stopping off" material to a titanium sheet according to a required pattern, and subsequently electrodepositing the platinum which adheres to the uncoated portions of the titanium sheet. Electrodes produced in this manner have, however, proved unsatisfactory when used in certain electro-chemical processes, owing to the unavoidable presence of a continuous, albeit very thin, film of oxide between the titanium and the platinum.

A roll bonding procedure in which strips of platinum are first placed in spaced grooves machined in a titanium

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sheet, and the assembly then rolled to effect bonding of the platinum strips to the titanium to form an inlay bi-metal sheet avoids the above disadvantages inherent in the electro-deposition method, as the severe deformation, resulting during rolling, tends to disrupt the oxide film and allows more intimate contact between the platinum and the titanium. This method, however, seldom results in an efficient bond at the edges of the grooves, owing to the fact that, during the rolling operation, only the forces due to lateral spread can act at the said edges.

We have found that the above disadvantages can be overcome in a simple manner. Broadly stated, our improved method comprises the steps of lightly adhering, for example by a tack or spot weld operation, one or more strips of noble metal or noble metal alloy to one or both faces of a refractory metal sheet or strip to form a composite bi-metal assembly; covering the assembly with, or encasing it in, a metal envelope or sheath to form an air-tight closure therearound; heating the so-encased assembly to a predetermined temperature and then applying pressure to the assembly simultaneously throughout the whole area of mutual contact of the constituent elements thereof to cause the noble metal strip or strips to become intimately bonded to, and lie flush or substantially flush with, the refractory metal sheet or strip, and subsequently removing the metal envelope or sheath.

The assembly may be heated to a temperature of 800°–950° C. preferably 850°–900° C. prior to the pressing operation and is maintained at this temperature during the pressing operation. A pressure of ½ to 5 tons/sq. in. will usually be found to be sufficient to effect bonding.

After removal of the envelope or sheath, the bonded assembly may be hot-rolled, for example by heating it to 700°–800° C. in an argon atmosphere before rolling to reduce it to substantially the required thickness and finally cold-rolled to final size, the noble metal strip or strips lying flush with the surface of the refractory metal base to form an inlay bi-metal sheet.

The refractory metal preferably consists of titanium, but other refractory metals, such as tantalum, niobium, vanadium and zirconium, may also be employed. In the application of the invention to the manufacture of electrodes, however, the use of titanium will generally be found to be the most satisfactory.

Whilst any suitable noble metal or noble metal alloy may be used to form the bonded strips, we have found platinum metal, or an alloy of platinum with one or more other platinum group metal or metals in which platinum predominates, to give the most satisfactory results particularly for the production of electrodes.

The envelope or sheath may be formed of nickel or mild steel sheet of a thickness of the order of 0.005 to 0.010 inch, such that it may readily be wrapped around the assembly and reduce the amount of entrapped air to a minimum.

The use of an envelope or sheath is essential in order to prevent absorption of oxygen, hydrogen or nitrogen by the refractory metal at the temperature of bonding, which is liable to cause an increase in hardness and render difficult the production of an efficient bond.

It will, moreover, be found desirable in practicing the invention to ensure that a uniform pressure is applied throughout the assembly as otherwise distortion may occur. This is particularly important in the case of the bonding of platinum or platinum alloy strip to titanium or zirconium by the method of the invention, as the latter forms an intermetallic compound with platinum at the bonding temperature, and if a uniform pressure is not applied, considerable variation in thickness of the inter-

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metallic layer may result. Such local thickening of the intermetallic layer will be found to be especially undesirable if the platinum or platinum alloy strip is less than about 0.001" in thickness.

The following is an example of the manner in which the invention may be carried out, as applied to the manufacture of a composite titanium-platinum electrode for electro-chemical purposes, it being understood that the invention is in no way limited thereto or thereby.

Example

A sheet of titanium of dimensions of 3" x 12" and 0.150" in thickness was first prepared by grinding the edges to remove burrs, followed by pickling in a cold aqueous solution containing 12% nitric acid and 12% hydrofluoric acid, and finally after the oxide had been removed, washing in water and drying.

Strips of platinum metal of 0.003" in thickness and 0.25" in width, which had previously been pickled in a hot aqueous solution of 50% aqua regia until the surface was lightly etched and then washed and dried, were then arranged at equal distances from, and parallel to, one another along the length of one side of the prepared titanium sheet and spot welded to the sheet, the welds being spaced from 4 to 6 inches from one another along the length of the platinum strips. Care must be taken, during this operation, to ensure that neither the platinum nor the titanium is handled with bare hands, as any finger prints are liable detrimentally to affect, or even to prevent, the subsequent bonding.

The so-formed assembly was then enclosed in a nickel sheath of about 0.005-0.010 inch thick which was tightly wrapped around the assembly in order to reduce the amount of entrapped air to a minimum, the contiguous edges of the sheath being double lapped and hammered so as to ensure an airtight seam. In order to avoid the possibility of the nickel envelope adhering to the platinum strips, a sheet of mica was placed between the strips and the sheath. If desired, instead of a mica sheet, brown paper or a stopping off compound, such as chromic oxide whitening, silicone varnish or asbestos powder, may be used.

The sheathed assembly was then placed in a furnace and heated to a temperature of 850° C. The furnace used comprised an hydraulically operated ram on which the assembly was placed and by the raising of which the assembly was introduced into the furnace, which had been heated to the required temperature. The furnace incorporated an anvil, housed in the roof of the furnace, by means of which pressure was applied to the assembly when the latter had reached a temperature of 850° C. A pressure of 11½ tons/sq. in. was applied for a period of about ½ hour, the temperature being maintained during this period at between 850° and 900° C.

At the end of this period the assembly was removed from the furnace and the envelope or sheath stripped off, the platinum strips having been firmly bonded to the titanium sheet. The assembly was then heated to 750° C. in an atmosphere of argon and hot rolled to within 0.010-0.015" of the required thickness.

Finally the composite sheet, after being degreased, pickled in a cold aqueous solution containing 12% of nitric acid and 12% of hydrofluoric acid, washed in water and dried, was cold-rolled to finished size with the platinum strips lying flush with the surface of the titanium sheet, thus forming a platinum-inlaid-titanium electrode.

If desired another refractory metal, such as tantalum, niobium, vanadium or zirconium may be used in place of titanium, and the inlay strips may be formed of a platinum-base alloy such as a platinum-rhodium alloy instead of platinum metal. The same temperature and pressure conditions may be employed to effect bonding, but the composition of the pickling solution employed prior to the welding operation and after hot rolling will vary according to the particular refractory metal used.

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The following pickling solutions are recommended for use with the following metals:

Refractory Metal:	Pickling solution
Tantalum-----	25% HF, 25% HNO ₃ , remainder H ₂ O.
Niobium-----	20% HF, 35% HNO ₃ , remainder H ₂ O.
Vanadium-----	50% HNO ₃ , remainder H ₂ O.
Zirconium-----	10% HF, 25% HNO ₃ , remainder H ₂ O.

It will be appreciated that the invention is applicable not only to the manufacture of electrodes, as particularly described above, but also to composite-bi-metal sheet or strip composed of a noble metal-stripped-refractory metal sheet or strip for use for any purpose for which such sheet or strip is suitable.

The invention, moreover, is intended to include within its scope composite metal sheet or strip when made by the method of the invention, and electrodes for electrochemical purposes or other articles when formed of or including such composite sheet or strip.

What we claim is:

1. A method of making a composite electrode for use in electro-chemical processes or for cathodic protection purposes which comprises the steps of spot welding a plurality of strips of platinum metal in parallel spaced relation to one face of a sheet of titanium to form a composite bi-metal assembly with said platinum metal strips lying superimposed on the surface of said sheet; air-tightly enclosing said assembly in a nickel sheath of about 0.005 to 0.010 inch thick by tightly wrapping said sheath around said assembly to reduce the amount of entrapped air to a minimum while locating a stop-weld material between said platinum strips and said nickel sheath, heating said assembly to a temperature of 850° C. and applying a pressure of 11½ tons/sq. in. to said heated assembly simultaneously and uniformly throughout the whole area of mutual contact of said platinum metal strips and said titanium sheet for a period of about ½ hour to force said platinum strips cleanly into the body of said titanium sheet and cause said platinum metal strips to become intimately bonded to, and lie flush with, said titanium sheet and in accurate delineation therewith, and subsequently stripping-off said nickel sheath.

2. A method according to claim 1 which includes the further steps of hot-rolling the bonded assembly to reduce it to substantially the required thickness and then cold-working the assembly to final size.

3. A method of making a composite platinum-titanium electrode for use in electro-chemical processes or for cathodic protection purposes which comprises the steps of lightly adhering at least one strip of platinum metal to the least one face of a sheet of titanium to form a composite bi-metal assembly with said platinum strip lying superimposed on said titanium sheet, encasing said assembly in a metallic sheath while locating a stop-weld material between at least said platinum strip and said sheath, heating said platinum-titanium assembly to a temperature within the range of 800-950° C. and applying pressure within the range from ½ to 5 tons/sq. in. to said heated assembly simultaneously and uniformly throughout the whole area of mutual contact of said platinum and titanium whereby said platinum strip is forced cleanly into the material of said titanium sheet and said platinum and titanium become intimately bonded together in mutually flush and accurately delineated relationship.

4. A method of making a composite inlay metal sheet or strip which comprises lightly adhering at least one strip element of metallic material selected from the group consisting of platinum metal and alloys of platinum with at least one other platinum group metal to at least one face of a base element of refractory metal selected from the group consisting of titanium, tantalum, niobium, vana-

dium and zirconium to form a composite bi-metal assembly with said strip element lying superimposed on said base element, encasing said assembly in a metallic sheath while locating a stop-weld material between at least said strip and said sheath, heating said bi-metal assembly to a temperature within the range of 800-950° C. and applying pressure within the range from ½ to 5 tons/sq. in. to the heated assembly simultaneously and uniformly throughout the whole area of mutual contact of the constituent elements thereof, whereby said strip element is forced cleanly into the material of said base element and said elements are intimately bonded to one another in mutually flush and accurately delineated relationship.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,115,702

December 31, 1963

Alfred Frank Scutt et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant (only), line 1, for "Alfred Frank Scutt" read -- Alfred Frank Scutt --; column 3, line 51, and column 4, line 36, for "11½ tons/sq. in.", each occurrence, read -- 1-1½ tons/sq. in. --; same column 4, line 54, for "the" read -- at --.

Signed and sealed this 5th day of May 1964.

(SEAL)
Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents