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METHOD FOR PROVIDING ON NIOBIUM OR NIOBIUM-ZIRCONIUM
ALLOYS METAL COATINGS BY GALVANIC ETCH-PLATING
Filed Nov. 20, 1968

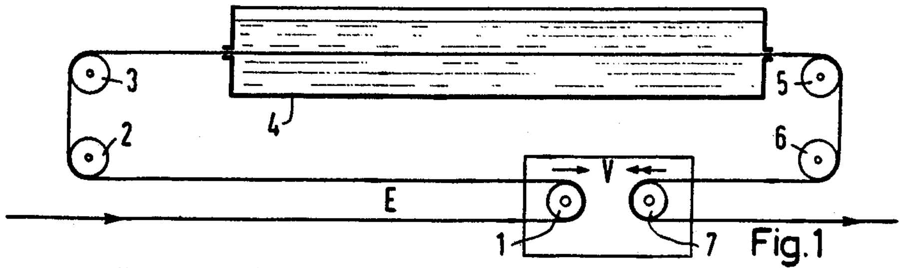

Fig.1

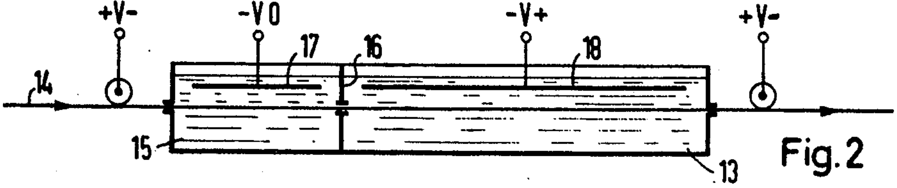

Fig.2

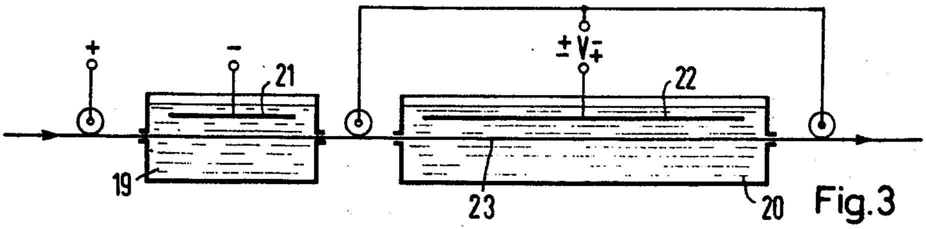

Fig.3

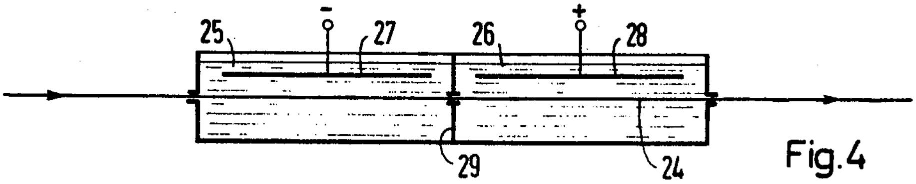

Fig.4

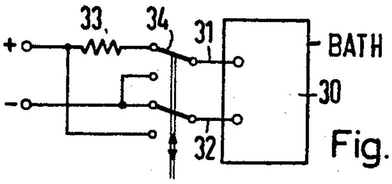

Fig.5

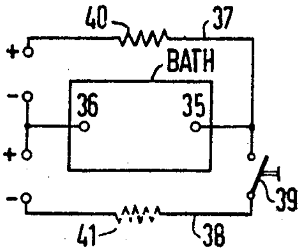

Fig.6

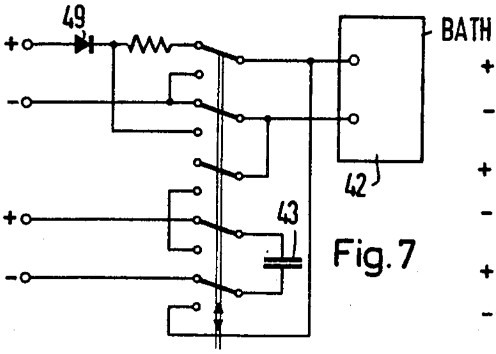

Fig.7

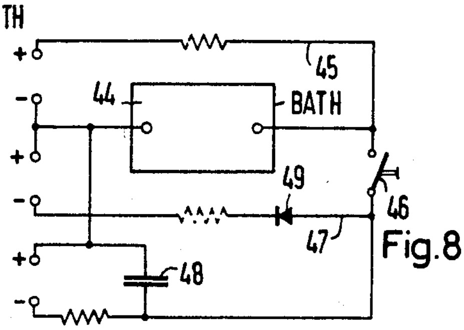

Fig.8

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# METHOD FOR PROVIDING ON NIOBIUM OR NIOBIUM-ZIRCONIUM ALLOYS METAL COATINGS BY GALVANIC ETCH-PLATING

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U.S. Cl. 204—32 14 Claims

## ABSTRACT OF THE DISCLOSURE

A method for providing on a superconductive metal, particularly niobium and alloys of niobium and zirconium, a coating of a metal such as nickel, copper, zinc, indium, tin or gold, with this coating being provided by a galvanic etch-plating process. According to the method the base metal which initially has been cleaned is anodically etched in an aqueous solution of hydrofluoric acid, ammonium fluoride, and a fluoride of the metal which is to form the coating. Then the polarity of the circuit is reversed so that the metal is then treated in the same solution cathodically. The reversal of polarity takes place with such rapidity that an inactivation of the exterior surface of the base metal cannot occur.

Our invention relates to a method for the galvanic etch-plating of metals or their alloys which can only be electroplated with difficulty, such metals being in particular made of superconductive materials.

It is already known that by galvanic plating it is not possible to achieve on a passive exterior metal surface a coating which will be reliably bonded to the metal. It has, therefore, already been proposed to eliminate the passivity of such metals for depositing a layer of a coating for plating material thereon by a suitable etching treatment. For example, such a treatment can take place with the use of strong acids, and in this case it is advisable, according to "Archiv fur Metallkunde" 1949, pages 38–42, to deposit either simultaneously with or immediately subsequent to the treatment with the strong acid an extremely thin layer of metal on the base metal in order to prevent a renewed passivity from occurring.

In U.S. Pat. 2,285,548 there is furthermore, a disclosure of a method for galvanically providing a copper coating on a chrome-containing alloy of iron and/or nickel, where initially, beside chemical etching in a hydrochloric acid nickel chloride solution there is a simultaneous anodic etching and then a cathodic deposition of a nickel layer in the same electrolyte bath. Alloys preliminarily treated in this way can, in accordance with this patent, be brought without any particular precaution into the galvanic bath.

However, experience has shown that many metals cannot be provided in this way with a coating which has a uniform, effective bond over the entire exterior surface of the base metal.

As is known from "Metalloberflache" volume 60 (1966), pages 441–444, during galvanizing of certain metals, such as, for example, titanium, zirconium, vanadium, niobium and tantalum, poor results are achieved because of the affinity of such metals for oxygen and their inclination to hydrogen adsorption or hydride formation.

It is accordingly a primary object of our invention to provide a method for coating a base metal of niobium or alloys of niobium and zirconium with a metal coating of nickel, copper, zinc, indium, or gold, by galvanic

etch-plating in such a way that the above drawbacks are avoided.

According to our invention, the base metal is initially anodically etched in an aqueous solution of hydrofluoric acid, ammonium fluoride and a fluoride of the metal which is to form the coating, and then in the same solution the metal is cathodically treated with the reversal of polarity being carried out in such a short time that an inactivation of the exterior surface of the base metal cannot take place.

Niobium and its alloy with zirconium have at the present time achieved a very great importance in the field of superconductors, and these metals are wound in wire or tape form in order to form superconducting magnet coils. In order to electrically protect such magnet coils, the wire or tape is first plated with a metal of good normal conductivity such as copper or silver. The protection is achieved as a result of the insulating action at temperatures below the typical temperature region as well as because of the good electrical and thermal conductivity of temperatures above the critical region. A magnetic coil can in such a case become normally conductive at a localized portion without being burned through as a result of such localized normal conductivity. As experience has shown, the galvanically deposited protective metal can only be of optimum effectiveness if it has an atomically-cohesive bond with the base metal.

It is accordingly an object of our invention to provide a method which will indeed achieve such a bond.

The fact that with the method of our invention it is possible to achieve a reliable bond of the protective metal coating on niobium or its alloys can only be considered as very surprising and unexpected. According to the state of the art such a result was not at all to be expected, because from "Metalloberflache," vol. 60 (1966), page 444, a known anodic preliminary treating in an aqueous hydrofluoric acid solution on such metals always resulted in a metal coating which had a very poor bond with the base metal. (Metal Finishing 52, 72/75 [1954].)

In the electrolyte bath used with the method of our invention, during the anodic treatment not only is the passive layer covering the base metal effectively attacked but also the resulting product is dissolved, so that the exterior surface is presented in an active condition for the cathodic deposition which takes place in the same bath or solution. By way of an extremely rapid reversal of polarity, the freshly manufactured exterior surface of the base metal which is in a condition of "statu nascendi" is so rapidly coated cathodically that no appreciable entry of hydrogen into the base metal can take place. The electrolyte baths used according to our invention are further characterized by the fact that the required metal which is in the solution to be cathodically deposited is dissolved in a complex form and a cementation during the etching phase does not take place.

Suitable fluorides of the metal which is to be deposited to form the coating are $NiF_2$, $AuF$, $CuF_2$, $SnF_2$, $ZnF_2$ and $InF_3$. The ratio of hydrofluoric acid to ammonium fluoride is preferably selected in such a way that in the electrolytic bath fluoride of the metal which is to be precipitated is present in an adequate concentration and an optimum galvanic deposition of the metal takes place.

The couterelectrodes can be made of the metal which is to be deposited, for example nickel and copper, or in the event that these metals are not anodically soluble in the electrolyte bath, insoluble anodes, graphite and carbon, for example, can be introduced.

The current densities which are to be used depend upon a particular metal which is to be deposited to form the coating as well as the base metal. During deposition of nickel on a base metal in the form of an alloy of 66% by weight niobium and 33% by weight zirconium, current densities of 8–35 a./dm.$^2$ have proved to be satisfactory, while during the deposition of a metal such as gold, to form the coating, it is preferable to use current densities between 2 and 7 a./dm.$^2$.

The current density during anodic etching can either be greater or also smaller than the current density which prevails during separation and deposition of the coating metal on the base metal. For an anodic etching of the above-mentioned niobium-zirconium alloy, current densities of 0.05–1.2 a./dm.$^2$, preferably, however, densities of from 0.1 to 0.9 a./dm.$^2$ are suitable.

The etch-plating is preferably carried out at room temperature, although higher temperatures can be used.

According to the simplest form of our invention, the metal body which is to be plated is situated within a container which contains the electrolyte liquid consisting, for example, of 10–12 g./l. $NH_4^+$, 20–25 g./l. $Ni^{2+}$, 40–50 g./l. $F^-$. The required counterelectrode can have a cylindrical configuration so that it will completely surround the base metal, although it is also possible to arrange two or more electrodes on both sides of the metal body. The base metal which initially is anodically connected into the circuit is switched cathodically into the circuit by rapid reversal of polarity, with anodic etching taking place in the first treatment phase and electroplating in the second phase. The reversal of polarity is carried out by way of rapidly operating contacts forming, for example, part of a magnetic switch, relay, transistor, or thyristor. The reversal time is between $10^{-3}$–$10^{-5}$ sec., but can be chosen so as to be even smaller. In order to avoid inactivation of the anodically etched exterior surface of the base metal, the time required for polarity reversal should, however, not be greater than 3 seconds.

Our invention is illustrated by way of example in the accompanying drawings which form part of this application and in which:

FIG. 1 is a schematic representation of one possible method of the invention for treating a base metal in the form of a wire or tape;

FIG. 2 is a schematic representation of another embodiment of the method of the invention;

FIG. 3 schematically represents a further embodiment of the method of our invention;

FIG. 4 shows a still further embodiment of a method of our invention; and

FIGS. 5–8 respectively illustrate various electrical circuits enabling the polarity reversal of the method of our invention to be carried out.

In the event that it is required to etch-plate wires or tapes, then the above-described embodiments of our invention can be altered in such a way that the metal which is to be plated is advanced in a stepwise, intermittent manner through the etch-plating bath. Thus, referring to FIG. 1, there is schematically illustrated therein an arrangement according to which this type of movement can be achieved. The wire which is to be treated is continuously fed to a roller **1** of a transporting head so as to form around this roller **1** the elongated supply loop E of the wire. From the roller **1** the wire is guided around the rollers **2** and **3** into the electrolyte bath **4**. The transporting head has the rollers **1** and **7** and moves in the opposed directions indicated by the arrows.

The wire stored in the loop E is advanced very rapidly into the electrolyte bath **4** during return of the transporting head to the left, as viewed in FIG. 1, so that as the supply loop E becomes shorter, the loop around the roller **7** becomes longer and the wire at the upper part of the loop E becomes rapidly drawn into the electrolyte bath in a horizontal direction extending toward the right, as viewed in FIG. 1, and the extent of movement of the transporting head is such that the length of wire introduced into the bath corresponds substantially to the length of the electrolyte bath **4**. This wire which is thus very rapidly introduced into the electrolyte bath is anodically loaded therein. Simultaneously the wire is of course withdrawn from the electrolyte bath around the guide rollers **5** and **6** and around the roller **7** of the transporting head. After etching and reversal of polarity the deposition of the metal takes place in the very same bath, and the time ratio of the anodic to the cathodic loading is determined in accordance with the metal which is to be deposited to form the coating as well as in accordance with the particular base metal. For deposition of a nickel coating on an alloy of 66% by weight niobium and 33% by weight zirconium, a time ratio of the anodic to the cathodic loading of 5 seconds/15 seconds has proved to be satisfactory.

During the etch-plating proces, the transporting head again moves slowly to the right so as to accumulate the new wire in the supply loop E, in preparation for repetition of the above steps during the next cycle.

According to a further embodiment of our invention, the above-described periodic galvanic etching and plating on the wire which moves in a stepwise manner can instead be carried out on a continuously moving wire. Because such a wire moves continuously a uniform covering of the base metal is not achieved and periodically occurring changes in the properties of the plating layer must be taken into consideration.

In accordance with FIGS. 2 and 3, however, the manner of operation can be carried out in such a way as to reduce these periodic fluctuations, so that the resulting plating or coating is adequate to meet the requirements of various uses to which the structure may be put.

According to the method of our invention which is illustrated in FIG. 2, there is a bath chamber **13** in which the etching and plating of a wire **14**, which moves in the direction of the arrow indicated in FIG. 2, takes place. In front of or ahead of the chamber **13** is a chamber **15** of the bath, and this preliminary chamber **15** contains the same electrolyte as the primary chamber **13**, the chambers **13** and **15** being separated by a partition **16** formed with an opening through which the wire **14** moves from the chamber **15** to the chamber **13**. The partition or wall **16** is made of an insulating material and separates the chambers **13** and **15** from each other, so that a flow of current through the electrolytes of both chambers is prevented to a large extent. The electrode **17** of the preliminary chamber **15** is connected into the circuit in such a way that during the etching phase this electrode **17** has a cathode polarity while in the plating phase the electrode **17** is neutral. By selecting a size for the chamber **15** which corresponds at least to the length of wire which enters into the chamber **15** during the cathodic precipitation phase, there is an assurance that plating takes place only on wire which has been preliminarily etched. The counterelectrode **18** is shown in the primary chamber **13** of the bath of FIG. 2.

As is apparent from FIG. 3, it is possible to completely separate and provide a space between the preliminary and main chambers of the electrolyte bath so that these chambers are mechanically as well as electrically separated from each other. The preliminary chamber **19** of FIG. 3, which serves for the preliminary anodic etching thus is spaced ahead of and separate from the primary chamber **20** which serves both for anodic etching and for cathodic deposition of the coating metal. In this case the preliminary chamber **19** and primary chamber **20** are respectively connected with different sources of current. The electrode **21** is connected into a circuit so as to have exclusively a cathodic action, while the electrode **22** in the primary chamber **20** of the bath **19**, **20** has its polarity reversed to act anodically and cathodically at the selected etch-plating frequency. In order to prevent inactivation of the exterior surface of the base metal formed by the wire **23**, the distance between the chambers **19** and **20** of the bath means **19**, **20** should be extremely small, on the order, for example, of a few cm. The wire **23** which continuously moves to the right, as viewed in FIG. 3, in the direction of the arrow, is thus treated in a manner similar to the wire **14** of FIG. 2, initially by being etched in the preliminary chamber of the bath means and then by being etched and plated in primary chamber of the bath means. The length of the bath means is predetermined in such a way that with selected linear speed of movement of the wire, a large number of operating cycles do not take place during the passage of the wire through the bath means, one cycle including one etching operation and one plating operation.

Thus, for example, if the time required for movement of a given section of wire which is to be electroplated through the bath means is 24 seconds, then a very reliably bonded nickel coating can be provided on the wire in such a way that the wire which is drawn into the primary chamber initially is treated anodically for 5 seconds at 0.4 a./dm.$^2$ and then upon reversal of polarity by means of an alternating current magnetic switch a cathodic treatment with 16 a./dm.$^2$ is carried out for 7 seconds. At the next reversal of polarity the cycle is repeated, so that during one passage through the bath means two cycles are carried out. The speed of movement of the wire in this case is approximately 24 m./h. The corresponding anodic treatment which takes place in the preliminary chamber has a duration of 9 seconds.

According to an embodiment of our invention which is particularly favorable from a structural point the etch-plating of wires and tapes can also be carried out in such a way that the wire or tape forms a neutral conductor of the circuit. In this case also the transporting of the wire which is to be etched and plated takes place continuously, while, in contrast with the above-described methods, the etching and plating takes place uniformly over the entire length of the wire. The continuously moving wire forms a bipolar conductor. The etching and plating take place at locations spaced from each other, with cells which are filled with the electrolyte. Thus, in FIG. 4 the continuously moving wire **24** forms a neutral wire of the circuit and moves in the direction of the arrow shown in FIG. 4 to the right, as viewed in FIG. 4. The etching cell **25** is situated in advance of the plating cell **26** in the direction of movement of the wire **24**. The electrode **27** situated in the cell **25** of the bath means of this embodiment is connected into the circuit exclusively in a cathodic manner while the electrode **28** in the cell **26** is connected into the circuit exclusively in an anodic manner. The cells or chambers **25** and **26** are separated from each other by a transverse partition or wall **29** made of an insulating material, plastic, for example, and formed with an opening through which the wire **24** can move.

An advantage of this method resides in the fact that the assembly does not require an electrical switching device and in addition a transporting unit such as the transporting head of FIG. 1 is not required to provide a supply loop from which the wire is advanced into the bath means. The adjustments of the different current densities in the electrolyte chambers **25** and **26** can be provided in a known way by way of a current divider in the etch-plating bath. However, a division of the current by way of one or more auxiliary anodes has also proved to be satisfactory. Of course, the auxiliary anodes when loaded with current are soluble in the electrolyte.

The anodically acting etching current density can furthermore be reduced by connecting the wire on the anode side with the cathode connections, which is to say through a current divider.

Thus, with the embodiment of FIG. 4 the reversal of polarity takes place simply by way of the partition wall **29** with its opening through which the wire **24** passes so that in the cell **25** there is one polarity and in the cell **26** there is a reversed polarity. Of course, in this way also an extremely rapid reversal of polarity is achieved.

With the schematically illustrated circuits of FIGS. 5–8 further explanation of the method of our invention is provided.

Thus, referring to FIG. 5, there is schematically illustrated therein an etch-plating bath **30** supplied with current for the wire which is to be treated by way of a conductor **31**, while a conductor **32** is provided for the counterelectrode which advantageously may be made of the metal which is to form the plating, and this counterelectrode thus may be made of nickel, for example. Electrical resistor **33** is provided for regulating the current density, and a switch assembly **34** is also shown, this assembly being, for example, a relay.

According to FIG. 6, the circuit may achieve the reversal of polarity by switching between a pair of current sources which respectively have opposed polarities. In this case, the electrolyte bath **36** provides anodic treatment of the base metal **35** within the electrolyte bath **36** initially by way of the current circuit **37**, and then by switching over to the current circuit **38** a reversal is made to cathodic treatment. The switch **39** is provided for switching between circuits **37** and **38**, and adjustments to achieve the optimum current density are provided by way of the resistors **40** and **41**.

According to a particularly favorable embodiment of our invention, the reversal of polarity **10** takes place, as illustrated in FIG. 7 by way of a pulsation of current resulting in a sharp rise in the cathodic current. In the case of FIG. 7 the base metal which is to be plated is initially treated anodically in the electrolyte bath **42**, in the same way as indicated in FIG. 5. Upon reversing of polarity, however, there is a simultaneous connection of the capacitor **43** into the circuit so that from the latter an impulse-type of charging is achieved. As a result of the steeply rising cathodic current achieved in this way a particularly effective bond of the plated metal is brought about.

According to a further embodiment of our invention, the type of circuitry which is used in FIG. 6 to achieve the reversal of polarity can also be provided with the pulsation-type of sharply increasing cathodic current brought about by way of connecting a capacitor into the circuit. A circuit of this type is shown in FIG. 8. The base metal which is in the electrolyte bath **44** of FIG. 8 is initially anodically treated through the circuit **45**. Upon reversal of polarity by way of the switching contact assembly **46**, the circuit **47** is rendered operative with an accompanying discharge of the capacitor **48**. This circuitry thus also is characterized by a steeply increasing cathodic current.

The blocking diodes **49** indicated in FIGS. 7 and 8 are provided to maintain the cathodic current pulses separate from the anodic current sources.

The following examples further serve to illustrate the method of our invention.

## EXAMPLE 1

Wire sections each having a length of ½ m. and made of NbZr 25 or NbZr 33 are tensioned in a suitable holding device and are electrically contacted at both ends. The oxide coated exterior surface of the wire as it comes from the wire-drawing operations is initially cleaned away mechanically by abrasive action and then chemically for a duration of one minute with a mixture of nitric acid, hydrofluoric acid, and water, this solution which thus provides the chemical pickling or etching having its components in a ratio of 5.4:1:3.6. The $NiF_2$ etching bath is composed of a mixture of 39 g. $NiF_2$, 35 g. $NH_4 \cdot HF_2$ and 6.6 ml. of 40% hydrofluoric acid, this mixture being diluted with distilled water up to 1.1. A nickel sheet serves as the counterelectrode. In this bath the wires which are to be plated are treated at a timing sequence of 5/15 to 15/5 seconds with anodic etching at 0.4 a./dm.$^2$ or after polarity reversal with 16 a./dm.$^2$. The reversal of polarity takes place either in the manner indicated in FIG. 5 and described above or in the manner indicated in FIG. 6 and described above, so that when the arrangement of FIG. 6 is used the opposed polarity is achieved by connecting a second current source into the circuit.

Then the thus-etch-plated wire is subjected for one minute to a preliminary galvanic copper plating in a conventional CuCN bath. The current density during this latter operation is 1 a./dm.$^2$. After an intermediate washing in water, a copper plating up to the desired layer thickness is achieved in a $CuSO_4$ bath (50 g. Cu/l.) with 5 a./dm.$^2$. The plating achieved in this way has a very strong bond with the wire core and provides a very effectively stabilized material for the construction of magnetic coils.

## EXAMPLE 2

A NbZr 33 wire of 0.5 mm. in diameter which has initially been sand blasted undergoes a cathodic degreasing and is chemically pickled or etched for one minute as in the case of Example 1 and then etch-plated after washing with distilled water. The wire in this example is continuously moved in the manner indicated in FIG. 2. The electrolyte bath is made up, as in the previous example, of $NiF_2$, $NH_4HF_2$ and hydrofluoric acid. During passage through the bath, 2½ cycles of nickel plating take place. Then cyanidic preliminary copper plating takes place for 75 seconds and then plating in copper sulphate bath having a 20% $CuSO_4$ solution is provided. The metallic layer which is achieved in this way has an extremely good mechanical bond.

The coatings provided with Examples 1 and 2 on niobium and alloys of niobium-zirconium have intermediate layers enabling the subsequently deposited galvanic coatings to have a very effective bond with the base metal over the entire exterior surface thereof. With many niobium alloys it can be of advantage to carry out the etch-plating of the invention a plurality of times.

## EXAMPLE 3

1 l. of an aqueous electrolyte contains 20 g. $ZnF_2$, 190 g. $NH_4F \cdot HF$, 25 ml. 40% hydrofluoric acid. The etching and plating are carried out at approximately 25° C. The current density during cathodic precipitation was 5 a./dm.$^2$ and during anodic etching 0.5 a./dm.$^2$. A zinc plate was introduced to act as the counterelectrode.

## EXAMPLE 4

1 l. of an aqueous solution contained approximately 120 g. $InF_3$ and 100 g. $NH_4F \cdot HF$. The current density during cathodic deposition was 18 a./dm.$^2$ and during etching 1 a./dm.$^2$. The etch-plating was carried out at room temperature and the counterelectrode was made of indium.

## EXAMPLE 5

1 l. of an aqueous electrolyte containing 150 g. $SnF_2$ and 120 g. $NH_4F \cdot HF$ was used. The current density during cathodic deposition was 3 a./dm.$^2$ and during etching 0.5 a./dm.$^2$. A tin plate was used as the anode. Etching and plating were carried out at room temperature.

## EXAMPLE 6

1 l. of an aqueous electrolyte contained 37 g. $CuF_2$, 100 g. $NH_4F \cdot HF$ and 60 g. 40% hydrofluoric acid. The current density during cathodic deposition was 1 a./dm.$^2$ and during anodic etching 0.1 a./dm.$^2$.

We claim:

**1.** In a method of providing a coating of a metal selected from the group consisting of nickel, copper, zinc, indium, tin, and gold on a base metal selected from the group consisting of niobium and alloys of niobium and zirconium, by galvanic etch-plating, comprising the steps of cleaning the base metal, then anodically etching the base metal in an aqueous solution of hydrofluoric acid, ammonium fluoride and a fluoride of the metal which is to form the coating, then reversing the polarity to treat the base metal cathodically in the same solution, while providing for the reversal of polarity a time which is so short that inactivation of the outer surface of the base metal does not take place.

**2.** In a method as recited in claim **1** and wherein the polarity reversal takes a maximum of three seconds.

**3.** In a method as recited in claim **2** and wherein the treatment takes place in an aqueous solution of $NiF_2$, $NH_4HF_2$ and hydrofluoric acid.

**4.** In a method as recited in claim **2** and wherein the etch-plating treatment takes place while the base metal is stationary.

**5.** In a method as recited in claim **2** and wherein the etch-plating takes place periodically on the base metal while the latter moves continuously.

**6.** In a method as recited in claim **1** and wherein the reversal of polarity is carried out by record switching operations.

**7.** In a method as recited in claim **1** and wherein there are two potential sources of opposed polarities with the reversal of polarity taking place by switching between the said sources.

**8.** In a method as recited in claim **1** and wherein the reversing of polarity is accompanied by discharge of a capacitor for intensifying the increase of cathodic current.

**9.** In a method as recited in claim **1** and wherein electrical resistors are used for providing different current densities during the anodic and cathodic treatments, respectively.

**10.** In a method as recited in claim **1** and wherein at least one auxiliary anode is used for providing different current densities for the anodic and cathodic treatments, respectively.

**11.** In a method as recited in claim **1** and wherein the electrical current is divided for achieving different current densities for the anodic and cathodic treatments, respectively.

**12.** In a method as recited in claim **1** and wherein prior to etch-plating of the base metal in said solution the base metal is moved to a preliminary chamber which is electrolytically connected with the etch-plating chamber where said solution is located and with an electrode in said preliminary chamber which is loaded only during the anodically effective current phase.

**13.** In a method as recited in claim **1** and wherein the base metal is preliminarily moved through a preliminary chamber situated ahead of the chamber where the etch-plating takes place and spaced from the latter chamber with the base metal being anodically pre-etched in said preliminary chamber.

**14.** In a method as recited in claim **1** and wherein the etching and plating respectively take place in separate chambers while the base metal moves continuously and is electrolytically connected into an electrical circuit as a bipolar conductor.

### References Cited

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,285,548 | 6/1942 | Wesley | 204—34 |
| 2,285,549 | 6/1942 | Wesley | 204—34 |
| 2,399,964 | 5/1946 | Ward | 204—34 |
| 2,711,389 | 6/1955 | Beach et al. | 204—32 |
| 2,873,233 | 2/1959 | Schnable | 204—32 |

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U.S. Cl. X.R.

204—28, 45, 141, 211, 228