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[54] **PROCESS FOR THE ELECTRODEPOSITION OF DUCTILE PALLADIUM AND ELECTROPLATING BATH USEFUL THEREFOR**

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[58] **Field of Search** ..... 204/47, 43 N, 44, 109

[56] **References Cited**

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[57] **ABSTRACT**

Non-porous ductile palladium is obtained by electrodeposition from a high chloride bath comprising:

about 16 to about 32 g/l of $Pd(NH_3)_2Cl_2$(palladosammine chloride), about 65 to 250 g/l of NH_4Cl and sufficient aqueous NH_3 to provide a pH of at least 8.8.

15 Claims, No Drawings

PROCESS FOR THE ELECTRODEPOSITION OF DUCTILE PALLADIUM AND ELECTROPLATING BATH USEFUL THEREFOR

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to processes for the electrodeposition of palladium and baths useful therefor.

2. Description of the Prior Art

Low-energy circuit contacts must be of low and stable contact resistance. The noble metals, such as gold and the metals of the platinum family which have low chemical reactivity and do not oxidize or form sulfides are commonly used in forming low-energy circuit contacts.

Due to the cost of the noble metals, low-energy circuit contacts are generally not made entirely of noble metals but, rather, the noble metal is electrodeposited on a base metal substrate.

Originally, gold was widely used for low-energy circuit contacts in view of its excellent properties. However, gold is soft and the commonly electrodeposited gold alloys suitable for use in low-energy circuit contacts have relatively poor resistance to wear.

Recently, palladium has increasingly been used to replace gold in forming low-energy circuit contacts on base metal substrates. Palladium is less expensive than gold, is relatively non-reactive, wears better than gold and has a density lower than that of gold so that for equal thicknesses the relative expense of the same thickness of metal contact can be decreased using palladium.

In electrodepositing palladium on a base metal substrate for electrical contact use two interrelated properties are required. Firstly, the palladium must be non-porous to prevent corrosion of the substrate which could cause the corrosion products to spread onto the contact surface where high electrical contact resistance and like problems could arise. Secondly, the electrodeposited palladium layer must be ductile. Following early prior art processes for electrodepositing palladium, stressed electroplates resulted which tended to crack, particularly during forming, and eventually cause the electrodeposited film of palladium to become porous, leading to device failure.

U.S. Pat. No. 1,981,715 Atkinson discloses a method and composition for electrodepositing ductile palladium upon a base metal substrate. However, a two compartment cell is required with anode and cathode compartments being separated by a diaphragm. The electrodeposition bath in this patent comprises four components: $Pd(NH_3)_2Cl_2$, NH_4Cl, aqueous ammonia and substantial proportions of $(NH_4)_2SO_4$, all constitutents being mandatory. Further, the NH_4Cl is used in relatively small proportions in the plating bath. U.S. Pat. No. 3,150,060 Fatzer discloses a similar method and composition, but the described method does not require the use of a two compartment cell.

U.S. Pat. No. 3,544,435 Angus also discloses a method for electrodepositing palladium. In the process described in this patent a single compartment cell may be used. The electrodeposition bath is rather specialized and consists of an aqueous ammoniacal solution of tetramminopalladous bromide having a pH of at least 9. The bromide moiety is mandatory and it is described

that deposits from otherwise similar baths, for instance where the bromide is replaced by chloride, are much less ductile and appreciably harder.

BRIEF SUMMARY OF THE INVENTION

One object of the present invention is to provide electrodeposited films of palladium which are highly ductile.

A further object of the present invention is to provide electrodeposited palladium films which are non-porous.

Yet another object of the present invention is to provide electrodeposited palladium films which are highly ductile, non-porous and which retain these properties for extended periods of time, thereby meeting all current state-of-the-art requirements for use as low-energy electrical contacts, low-energy electrical connectors, and the like.

Still yet a further object of the present invention is to provide electrodeposited palladium films of high electrical conductivity and high resistance to both corrosion and mechanical wear.

Still yet another object of the present invention is to provide electrodeposited palladium electrodeposits which are sufficiently ductile to be deformed during manufacturing or in service without cracking.

Another object of the present invention is to provide non-porous, highly ductile palladium electrodeposits which exhibit low internal stresses.

These and other objects of the present invention are reached by electrodepositing palladium from a high chloride aqueous electrodeposition bath which contains $Pd(NH_3)_2Cl_2$, NH_4Cl and aqueous ammonia.

DETAILED DESCRIPTION OF THE INVENTION

The aqueous electrodeposition bath of the present invention comprises three mandatory constituents: $Pd(NH_3)_2Cl_2$, NH_4Cl and aqueous ammonia.

When the $Pd(NH_3)_2Cl_2$ is present in an amount from about 16 to about 32 g/l, preferred non-porous and highly ductile electrodeposited palladium films are obtained. When the $Pd(NH_3)_2Cl_2$ is excessively below about 12 g/l, the electrodeposited palladium film tends to be dark and porous. On the other hand, if the $Pd(NH_3)_2Cl_2$ concentration is excessively above about 32 g/l, the "drag-out" losses of palladium increase without compensatory benefits in the characteristics of the electrodeposited palladium film. While commercially undesirable, if increased drag-out losses are acceptable to the processes greater amounts of $Pd(NH_3)_2Cl_2$ can be used.

Electrodeposition within the most preferred range set out above offers a further advantage: there is a lowered tendency for preferential palladium deposition onto raised surface irregularities on the base metal substrate, a requirement of some electrical contacts.

The electrodeposition bath of the present invention generally contains NH_4Cl in an amount of from about 65 to about 250 g/l, more preferably from about 130 to about 250 g/l, with aqueous ammonia being present in an amount sufficient to provide a pH of at least about 8.8 to the bath. The aqueous ammonia is conveniently added as 28~30 wt. percent aqueous ammonia. Generally from about 75, more preferably 100, to about 150 ml of 28~30 wt. percent aqueous ammonia is added. Aqueous ammonia solutions of greater or lesser concentrations can be used so long as an equivalent amount of ammonia per se is provided.

It is important that the pH of the electrodeposition bath of the present invention be maintained at above about 8.8. This value is important in obtaining a nonporous, highly ductile film of palladium since at pH's excessively lower than about 8.8, e.g., 6.0~7.5, an insoluble salt of palladium may precipitate, particularly at the surface of the anode, during electrodeposition.

Since the electrodeposition process of the present invention is typically conducted in a system open to the atmosphere, a pH greatly in excess of about 10 is avoided primarily because at such pH's high evaporation losses of ammonia are encountered, requiring excessive make-up amounts of ammonia which is not necessary by practicing the process of the present invention at lower pH's. Most preferably the pH is maintained within the range of pH 8.8 to pH 9.2 during electrodeposition.

As indicated above, during the electrodeposition process of the present invention free ammonia is liberated and escapes from the electrodeposition bath. For this reason, sufficient aqueous ammonia is generally introduced into the bath prior to electrodeposition so as to maintain the pH within the above bounds.

Palladium is also lost from the bath by electrodeposition thereof. Accordingly, $Pd(NH_3)_2Cl_2$ is also generally introduced into the bath in amounts sufficient to maintain the $Pd(NH_3)_2Cl_2$ concentration within the range of from about 16 to about 32 g/l. The $Pd(NH_3)_2Cl_2$ is preferably added dissolved in aqueous ammonia, the latter also contributing to establish the pH of the electrodeposition bath.

Chloride is introduced in the electrodeposition of the present invention from two sources during electrodeposition: from the $Pd(NH_3)_2Cl_2$ as it is consumed and from the NH_4Cl. It is preferred that the total amount of free chloride in the plating bath be from about 50 to about 200 g/l, with a most preferred minimum chloride content being about 80 g/l. Since free chloride will accumulate in the system during electrodeposition, generally the total amount of free chloride present in the electrodeposition bath is near the lower end of this range at the initiation of plating with plating being terminated prior to reaching free chloride values substantially in excess of about 200 g/l. The upper limit is imposed by the saturation point of NH_4Cl; crystallization of NH_4Cl should be avoided during the electrodeposition process of the present invention. At free chloride values substantially below 50 g/l the electrodeposited palladium film shows a tendency towards decreased ductility.

In accordance with the present invention a single compartment cell may be used or a cell provided with a diaphragm dividing the cell into compartments may be used. Generally, a compartmentalized cell is not used because this leads to a high voltage drop, requiring excessive power. It is a substantial advantage in the present invention that it can be practiced without the use of a diaphragm as is required, for example, in prior art processes as typified by U.S. Pat. No. 1,981,715 Atkinson, discussed above.

In accordance with the present invention the workpiece being plated with palladium comprises the cathode. The form or shape of the cathode is not limited in any manner.

The anode can be any non-reactive metal, and typically is a noble metal. The noble metal can be used as the anode per se or, more commonly, is plated upon a less expensive metal. For instance, on a commercial scale the anode will typically be titanium plated with platinum.

Appropriate electrical connections are provided between the cathode and anode in a manner known to the art to conduct electrodeposition.

The electrodeposition bath of the present invention is merely formed by mixing the components with water. For instance, aqueous ammonia is mixed with an equal volume of water and the $Pd(NH_3)_2Cl_2$, commonly available in dry form, dissolved therein, whereafter NH_4Cl and additional water are added to bring the volume of the electrodeposition bath to that required for a process run.

The temperature of electrodeposition is not especially important in the present invention. Generally, operation is at room temperature to about 90°F. Higher temperatures are generally not used for the practical reason that with a system open to the atmosphere this will lead to excessive ammonia volatilization. Lower temperatures can be used, but nothing is to be gained by cooling the system, from the viewpoint of product benefits.

The electrodeposition process of the present invention is typically practiced at normal pressure. Sub- or super-atmosphere pressures can be used but such are not necessary. In fact, sub-atmospheric pressure will generally be avoided since this leads to higher volatilization of ammonia. If one wishes to recover and recycle ammonia, of course, such can be used.

The apparent current density during electrodeposition is most preferably maintained within the range of from about 0.2 to about 2 amps/sq. dm. in commercial operation. By varying other parameters it is, of course, possible to electrodeposit at apparent current densities outside this range, but little is to be gained thereby in the sense of improved product characteristics.

When the preferred compositional bath parameters heretofore discussed are observed during electrodeposition, at apparent current densities substantially less than about 0.2 amps/sq. dm., the electrodeposited palladium film generally tends to become grey and porous. As apparent current densities increasingly in excess of about 2 amps/sq. dm. are used the electrodeposited palladium film generally becomes greyish, then black and porous and finally whiskers form.

In barrel plating it is most preferred that the apparent current density be within the range of from about 0.2 to about 0.3 amps/sq. dm. On the other hand, with still or rack plating it is most preferred that the apparent current density be maintained within the range of from about 0.50 to about 2.0 amps/sq. dm., most preferably 0.65 to 1.2 amps/sq. dm.

The electrodeposition process of the present invention can be practiced with or without agitation. In barrel plating, of course, agitation is inherent from the rotation of the barrel. The advisability of agitation for electrodeposition onto a particular workpiece is determined by factors well known in the electrodeposition art, and is a secondary consideration in the electrodeposition.

The electrodeposition bath of the present invention generally will contain no additives, though such can be used if they do not adversely influence the electrodeposition bath. Some care must be taken in this regard since classic additives such as saccharin and the like actually have a detrimental influence on the porosity of the electrodeposited palladium film. Further, the presence of certain organic materials in the electrodeposi-

tion bath, for instance CN ions, harm ductility and they should be avoided. Non-detrimental buffers can be used, but are generally unnecessary as the electrodeposition bath of the present invention exhibits a self-buffering effect.

As earlier indicated, one advantage of the present invention is that the electrodeposition of palladium as a non-porous, highly ductile film can be achieved with an electrodeposition bath substantially free of $(NH_4)_2SO_4$. While $(NH_4)_2SO_4$ can be present and electrodeposition in accordance with the present invention will proceed, if $(NH_4)_2SO_4$ is present the electrodeposition conditions must be much more critically controlled and no matter how carefully conditions are controlled it is impossible to obtain an electrodeposited palladium film having a ductility which is as high as a comparable system which is free of $(NH_4)_2SO_4$.

The electrodeposition of palladium in accordance with the present invention can be carried out on any conductive material or metal which does not adversely influence the electrodeposition bath of the present invention. For instance, in forming electrical contacts or connections some of the most commonly used base substrate metals are nickel, copper, beryllium-copper alloys, brass and the like. Electrodeposition in accordance with the present invention can successfully be carried out on all such materials.

During the electrodeposition of palladium in accordance with the present invention the plating rate is substantially proportional to current density over all plating ranges up to and including about 2.5 amps/sq. dm. The cathode efficiency is substantially equal to one. While not limiting, typical plating rates vary from about 0.5 micron per minute with still or rack plating down to about one-twentieth of a micron per minute with barrel plating.

In accordance with the present invention non-porous, highly ductile palladium films can be formed on base metal substrates with thicknesses as small as about 1 micron or with thicknesses as large as 15 microns or greater. At thicknesses substantially less than about 1 micron, the palladium film will have a tendency to become porous. Thicknesses greater than 15 microns can be obtained merely by increasing the plating time, but generally such greater thicknesses will not be used considering the cost of palladium. However, where a contact or the like must illustrate a sliding function (good friction wear), one might wish to form electrodeposited palladium film substantially in excess of 15 microns. For instance, thick palladium electrodeposits will often be used for the components of slip ring contacts which often have to withstand severe wear-inducing conditions in service.

The present invention provides several substantial advantages over the prior art:

Firstly, by the use of extremely high proportions of NH_4Cl present invention uses NH_4Cl in an amount of approximately tenfold that generally suggested by the prior art, the prior art, in fact, generally teaching one to avoid high amounts of NH_4Cl due to inherent chloride build-up during electrodeposition) it is possible to utilize a system free of $(NH_4)_2SO_4$, whereby electrodeposited palladium films which are much more ductile than those obtained in accordance with prior art procedures can be obtained. This statement holds true even with respect to prior art procedures specifically directed to obtaining ductile palladium films.

Secondly, at substantially all thicknesses it is possible to obtain a highly ductile palladium film which is non-porous. As earlier indicated, many of the early palladium deposition processes yielded porous films.

Having thus generally described the invention, the following specific example is given to illustrate preferred embodiments thereof.

EXAMPLE 1

An electrodeposition bath for barrel plating was formed of the following components at the recited proportions:

$Pd(NH_3)_2Cl_2$	:	22 g/l
NH_4Cl	:	125 g/l
Aqueous ammonia (30 wt. %) to provide a pH of 8.9		
Deionized water to make 1 liter		

Using conventional state-of-the-art electrodeposition apparatus, plating was conducted upon a nickel pin-type male electrical connector as the cathode using platinum coated titanium as the anode in a non-compartmented cell under the following conditions:

Apparent current density:	0.24 amp/sq. dm.;
Temperature:	room temperature;
Pressure:	normal pressure;
Time:	35 minutes;
Plating rate:	670 A/minute;
Thickness of electrodeposited palladium film;	2.4 μ.

The electrodeposition was a barrel deposition, using a perforated barrel 4 inches in diameter by 6 inches in length in a tank containing 20 liters of the above described electrodeposition bath. The barrel was rotated about its axis at 15 rpm throughout the electrodeposition. The pH was adjusted to about 9.0 one hour prior to electrodeposition by the addition of 28 wt. percent aqueous ammonia to the plating bath. The addition of aqueous ammonia is typically required with this apparatus after two such electrodeposition runs or after permitting the bath to stand idle for more than 24 hours.

The electrodeposited palladium film was non-porous and highly ductile.

EXAMPLE 2

An electrodeposition bath for still plating was formed of the following components at the following proportions:

$Pd(NH_3)_2Cl_2$	:	25 g/l
NH_4Cl	:	169 g/l
Aqueous ammonia (30 wt. %) to provide a pH of 9.0		
Deionized water to make 1 liter		

Using conventional state-of-the-art electrodeposition apparatus, plating was conducted upon a nickel-iron alloy substrate as the cathode using platinum coated titanium as the anode under the following conditions:

Apparent current density:	0.65 amp/sq. dm.;
Temperature:	room temperature;
Pressure:	normal pressure;
Time:	10 minutes;
Plating rate:	1,780 A/minute;
Thickness of electrodeposited palladium film:	2 μ.

The bath was not artificially agitated during the electrodeposition.

The electrodeposited palladium film was non-porous and highly ductile.

While the invention has been particularly shown and described with reference to the preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. An aqueous electrodeposition bath for electrodepositing non-porous, ductile palladium which comprises:

from about 16 to about 32 g/l $Pd(NH_3)_2Cl_2$;

from about 65 to about 250 g/l of NH_4Cl; and

aqueous ammonia to provide a pH of at least about 8.8.

2. The aqueous electrodeposition bath of claim **1** which consists essentially of $Pd(NH_3)_2Cl_2$, NH_4Cl and aqueous ammonia.

3. The aqueous electrodeposition bath of claim **2** where the pH of the electrodeposition bath is from about pH 8.8 to about 9.2.

4. The aqueous electrodeposition bath of claim **3** where the NH_4Cl is present in an amount of from about 130 to about 250 g/l.

5. The aqueous electrodeposition bath of claim **2** where $Pd(NH_3)_2Cl_2$ is present in an amount of from 17 to 27 g/l.

6. A method for electrodepositing non-porous, ductile palladium on a substrate which comprises

immersing an anode in an aqueous electrodeposition bath which comprises:

from about 16 to about 32 g/l $Pd(NH_3)_2Cl_2$;

from about 65 to about 250 g/l of NH_4Cl; and

aqueous ammonia to provide a pH of at least about 8.8,

immersing the substrate to be coated in said electrodeposition bath; and

applying a potential difference between the anode and substrate to conduct the electrodeposition of palladium.

7. The method of claim **6** where the electrodeposition bath consists essentially of $Pd(NH_3)_2Cl_2$, NH_4Cl and aqueous ammonia.

8. The method of claim **7** where electrodeposition is carried out at an apparent current density of from about 0.2 to about 2.0 amps/sq. dm.

9. The method of claim **8** where the free chloride content of the electrodeposition bath is maintained within the range of from about 50 to about 200 g/l during the electrodeposition.

10. The method of claim **9** where the $Pd(NH_3)_2Cl_2$ concentration is maintained within the range of from about 16 to about 32 g/l during the electrodeposition.

11. The method of claim **8** wherein the electrodeposition is a rack or still electrodeposition carried out at an apparent current density of about 0.5 to about 2.0 amps/sq. dm.

12. The method of claim **11** where the electrodeposition is without agitation.

13. The method of claim **8** where the electrodeposition is a barrel electrodeposition carried out at an apparent current density of about 0.2 to about 0.3 amp/sq. dm.

14. The method of claim **7** where $Pd(NH_3)_2Cl_2$ is present in an amount of from 17 to 27 g/l.

15. The method of claim **6** where the electrodeposited palladium is at least about 1 μ thick.

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