

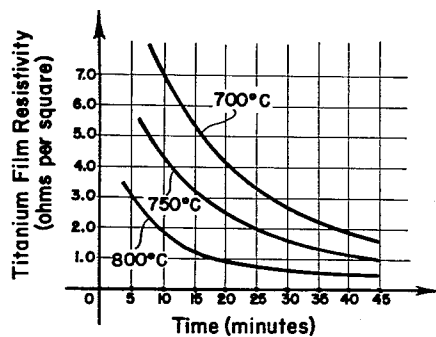
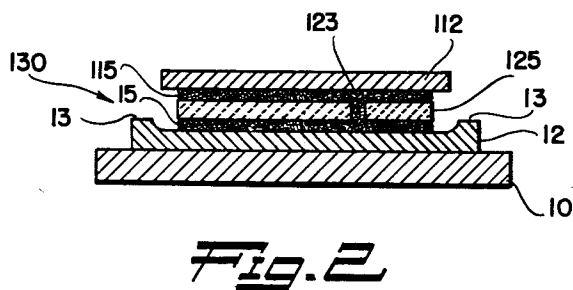
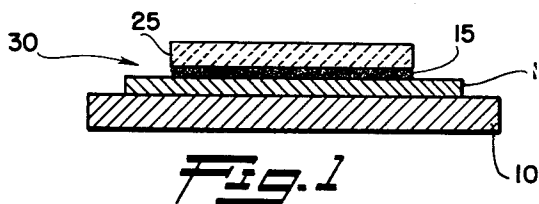
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R. A. QUINN ET AL

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METHOD OF COATING A BODY WITH TITANIUM AND RELATED METALS

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INVENTORS

ROSS A. QUINN

ROBERT F. KARLAK

By *George C. Sullivan*
Agent

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METHOD OF COATING A BODY WITH TITANIUM AND RELATED METALS

Ross A. Quinn, Palo Alto, and Robert F. Karlak, Sunnyvale, Calif., assignors to Lockheed Aircraft Corporation, Burbank, Calif.

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This invention relates to an improved method of coating a body with titanium and related metals which is relatively simple and inexpensive and can be advantageously adapted to semi-automatic and mass production techniques.

It has been known for some time that metals like titanium, zirconium, hafnium and uranium possess certain desirable properties which make them useful for plating various surfaces. It has recently been discovered that the use of such metal coatings, particularly titanium, on a suitable substrate also offers several important advantages for printed and integrated electronic circuitry applications. It is with regard to the coating of titanium for such applications that the present invention is generally directed, but it is to be understood that the invention is also applicable for other purposes, and may be applied for coating zirconium, hafnium and uranium as well as titanium.

Coating with titanium and the related metals of zirconium, hafnium and uranium in general has presented a considerable problem because of their tendency to oxidize in air, particularly at elevated temperatures. In order to prevent this unwanted oxidation, processes for coating these metals are complicated by the necessity of taking precautions against oxidation. Examples of known methods for coating titanium and these related metals are disclosed in U.S. Patent No. 2,732,321 and U.S. Patent No. 2,746,888. The method of the former patent involves immersing the body to be coated into a fused inorganic material bath having a temperature between about 700° and 1000° centigrade, bringing a source of titanium zirconium, hafnium and uranium into close proximity with the surface within the heated bath and maintaining the bath temperature long enough to form an appreciable coating of the metal on the surface. The latter patent involves immersing the solid body into a molten salt bath of one or more alkali or alkaline earth metal halides and divalent titanium for a period of time and at a temperature sufficient to deposit a coating of titanium on the body.

In the above-mentioned patents, the baths serve both as a flux to protect the metal coating which forms on the body from oxidation and as a heating medium. From an examination of the methods disclosed by these patents it will readily be appreciated that these methods, particularly the necessity of immersing the surface to be coated in a heated bath, would be expensive and unsuited for mass production techniques and thereby limit any practical use of either of these titanium coating methods for printed or integrated electronic circuit applications.

Accordingly, it is the broad object of the present invention to provide a simplified method for coating a body with titanium, zirconium, hafnium or uranium.

A more specific object of this invention is to provide a simplified method for forming a thin uniform film of titanium on a substrate.

Another object of this invention is to provide a simplified method for forming a thin uniform film on the flat surface of a refractory substrate in a manner which is readily adaptable for semiautomatic and/or mass production techniques.

Still another object of this invention is to provide a simplified method for simultaneously forming a thin uni-

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form film of titanium on both sides of a refractory substrate and also on the interior surfaces of one or more apertures in the substrate.

A further object of this invention is to provide a new and simple method of forming a thin alloy film.

In a typical embodiment of the invention the above objects are realized by a method in which heat is applied to a three-layer sandwich assembly having one outer layer of titanium or titanium alloy, the other outer layer of a ceramic substrate whose surface is to be coated with titanium and an inner layer sandwiched between these two outer layers of a thin layer of a salt comprising any one or a mixture of the alkali or alkaline earth metal halides. Contrary to what might be expected from previous considerations concerning the oxidation of titanium, it has been discovered that if this simple sandwich assembly is heated in air to the necessary high temperature, a uniform thin film of titanium can be successfully deposited on the substrate without the occurrence of deleterious amounts of oxidation. This discovery is important because the bath treatment required in the methods of the two aforementioned patents is now no longer necessary, the much more convenient sandwich assembly making possible a greatly simplified method of coating titanium which readily lends itself to semi-automatic and/or mass production techniques.

The specific nature of the invention, as well as other objects, uses and advantages thereof, will clearly appear from the following description and from the accompanying drawing in which:

FIG. 1 is a cross-sectional view of a three-layer sandwich assembly which is employed for coating a thin titanium film on one side of a suitable substrate in accordance with the invention.

FIG. 2 is a cross-sectional view of a five-layer sandwich assembly for coating a thin titanium film on both sides of a suitable substrate and on the interior of a hole in the substrate, in accordance with the invention.

FIG. 3 is a graph showing the resistivity of the titanium film obtained on a substrate as a function of the time of treatment for three temperatures to which the sandwich assembly is subjected.

Like numerals designate like elements throughout the figures of the drawing.

Now referring to FIG. 1, a three-layer sandwich assembly 30 rests on a support 10 which may suitably be made of graphite. One outer layer of the sandwich assembly 30 is a sheet 12 of titanium or titanium alloy, the other outer layer 25 is a substrate whose inner surface is to be coated with titanium, and the inner layer 15 is a salt which may be any one or a mixture of the alkali or alkaline earth metal halides. The substrate 25 may be any of a variety of materials such as fused silica, quartz, glass, alumina, magnesium silicate, magnesium oxide and the like.

In order to provide the thin layer of salt 15 between the substrate 25 and the titanium 12 a variety of techniques may be employed. The salt may be coated onto the titanium 12 and/or substrate 25 either by dipping into a molten salt bath, by spraying on a solution containing the salt, by melting on granules of the salt, or by spreading on a fine powder of the salt.

In accordance with the invention, the sandwich assembly 30 shown in FIG. 1 is now subjected to heat in an air environment which may be provided by any convenient means such as a furnace, or just an open flame. The sandwich assembly 30 is heated to a sufficient temperature to cause the salt 15 to melt and the titanium to deposit on the surface of the substrate 25. The thickness of the titanium film coated on the substrate 25 will be dependent upon the temperature to which the assembly 30 is

heated and the time for which the assembly 30 is maintained at this temperature.

We have discovered that if a liquid salt boundary is maintained between the titanium 12 and the substrate 25 during the titanium deposition process when the salt 15 has melted, the melted salt itself will serve as a sufficient barrier to prevent oxidation from deleteriously interfering with the deposition of titanium on the substrate. Only sufficient salt need be provided, therefore, to achieve this liquid salt boundary, which means that only a very thin layer of salt 15 is actually necessary and may be of the order of only a few molecular layers. The molten salt in the sandwich assembly 130 thus serves three purposes. It not only serves as the solution needed for the deposition process, but it also serves as a separator, and further as a barrier to the introduction of oxidizing air.

Because the surface tension of the molten salt will tend to maintain a liquid boundary between the titanium 12 and the substrate 25, even in the presence of excessive run-off or squeezing thereof, satisfactory results may be obtained with the sandwich assembly 30 in any position, even vertical. However, the dripping and run-off of salt is generally undesirable because it may get on apparatus or other units. It is preferred, therefore, that the salt layer be horizontal during heating, in which case the salt remains essentially between the sandwich and no clamping means need be provided. If the sandwich is vertical some means must be provided for holding the sandwich together during heating. Obviously, the weight or clamping should not be so great as to squeeze so much of the melted salt out of the sandwich that a liquid boundary is not obtained during the titanium deposition process. Because of surface tension, however, this is usually no real problem in actual practice as long as the sandwich remains together.

Of course, until the salt melts, some air may be introduced into the system, but it has been found that a salt of one or a mixture of the alkali or alkaline earth metal halides melts at a sufficiently low temperature to prevent any deleterious oxidation of the titanium surface from taking place. Once the temperature is high enough so that oxidation could proceed rapidly, the salt has melted and the liquid boundary it forms bars the introduction of air.

In actual practice satisfactory titanium deposition has been accomplished using thin layers of titanium and alumina substrate from about .010 inch to one inch thickness and uniformly spreading on the salt 15 over the titanium layer 12 as a fine powder until the salt is observed to just cover the area on the titanium corresponding to the area on the surface of the substrate 25 which is to be coated. The salt thickness is then ordinarily less than $\frac{1}{32}$ inch. Usually, salt thicknesses too much greater than $\frac{1}{8}$ inch are not desirable since excessive running of the salt may occur.

After the sandwich assembly 30 has been subjected to the temperature and for a time sufficient to produce a titanium coating of a desired thickness, the assembly 30 is cooled, separated and the titanium coated substrate then washed in water to remove any adherent salt. During cooling the molten salt 15 continues to bar the introduction of oxidizing air and becomes solid at a sufficiently low temperature so that the limited air which is then introduced when the salt is in solid form produces a negligible effect.

It should be noted that the thickness of the salt layer 15 is not critical since the important criterion is the maintenance of a liquid boundary between the layers of titanium and substrate after the salt melts. Excessive amounts of salt will not interfere with the deposition process, but may cause the salt to run to an extent which will detract from the overall convenience and suitability of the method for semiautomatic or mass production techniques.

In FIG. 2 a five-layer sandwich assembly 130 is shown

which permits both sides of a substrate 125 to be coated with titanium at the same time. As in FIG. 1 a thin layer of salt 15 is sandwiched between a layer of titanium 12 and a layer of substrate 125 so as to permit the bottom surface of the substrate 125 to be coated with titanium as described in connection with FIG. 1. Now, in order to permit the top surface of the substrate 125 to simultaneously be coated with titanium, a second thin layer of salt 115 is sandwiched between the top surface of the substrate 125 and a second titanium layer 112 as shown in FIG. 2. When this five-layer sandwich assembly 130 is subjected to heating both surfaces of the substrate 125 will be coated with titanium of substantially the same thickness, since both are subjected to the same temperature for the same time. When the salt 15 and 115 melts, liquid salt boundaries are provided between both surfaces of the substrate 125 and its respective titanium layer 12 or 112 to prevent sufficient air from being introduced into the system to deleteriously interfere with the titanium deposition process. Once the salt 15 and 115 melts, the substrate 125 effectively floats in the liquid salt between the outer titanium layers 12 and 112. As in the three-element sandwich assembly of FIG. 1, the weight of the various layers should not be such as to squeeze out so much salt that a liquid boundary would not be obtained during deposition. Since there is a greater possibility of running in the sandwich assembly 130 of FIG. 2, because of the larger amount of total salt, it may be desirable to provide short stubs 13 on the titanium layer 12 to prevent run-off.

While practicing the method of this invention using the sandwich assembly 130 of FIG. 2, it was discovered that apertures in the substrate 125, such as the aperture 123, also have their interior surfaces coated with a film of titanium during the process. If desired some salt could be provided in the aperture, but satisfactory coating of apertures or cavities of small depth has been accomplished without doing so, since sufficient melted salt flows into the aperture during the deposition process. If salt is provided in the aperture, depths up to one-half inch can be satisfactorily coated. Also, since the time and temperature of treatment is the same for the entire assembly 130, a substantially uniform coating of titanium is obtained throughout. The ability to coat the interior surfaces of apertures is of considerable importance in the fabrication of structures for printed or integral electronic circuitry, since electrical contact can then be conveniently provided between points on opposite sides of the substrate by means of a hole in the substrate. It should be noted that apertures in a substrate can also be coated with titanium by means of the simple sandwich assembly 30 of FIG. 1.

A more complete understanding of the present invention may now be obtained from the following illustrative example. Referring to FIG. 1, a salt mixture 15 is selected essentially consisting of 22 mole percent NaCl, 53 mole percent KCl, and 25 mole percent KI. This salt mixture is then ground in a mortar and pestle to a fine intimately mixed powder which is dried for at least 24 hours before use at 100° centigrade in a vacuum oven. The powder is then applied to the titanium sheet 12 by spreading it uniformly through a fine mesh screen until the powder appears to just cover the surface of the titanium 12. The resultant layer of the powder is then of the order of $\frac{1}{32}$ of an inch thick. The substrate 25 to be coated is now placed on the fine powder and the sandwich assembly 30 is placed in a furnace at the temperature and for the time required to produce the desired thickness of titanium coating. FIG. 3 is a graph illustrating the resistivity of the resultant titanium film obtained in ohms per square (which is a measure of film thickness) as a function of the treatment time for three furnace temperatures.

As mentioned initially, the process of the invention is also useful for coating substrates of other than refractory material. As a result of experiments in this direction, a

new method has been discovered for forming a thin uniform film of an alloy of copper and titanium, zirconium, hafnium or uranium on the surface of a body. Such an alloy film is most difficult to produce by presently known techniques.

In accordance with this method, a thin film of a copper-titanium alloy is formed on the surface of a body as follows. The body is first coated with a thin film of copper by any well known method, for example vacuum evaporation. The copper-coated body is then subjected to the titanium deposition treatment using a sandwich assembly as described herein. It has been found that during this treatment, alloying and deposition occur simultaneously so that the final surface film obtained is not a layer of titanium but in fact is an alloy of copper and titanium. The percentage composition of the two materials is easily controlled by controlling the deposition time of the copper and titanium deposition processes. Using this method a thin homogeneous film of a 50-50 percent copper-titanium alloy having a thickness of the order of 20,000 angstroms has been formed on an alumina substrate by first evaporating onto the substrate a 10,000 angstrom film of copper, and then subjecting this copper film to the sandwich titanium deposition process described herein until a final thickness of about 20,000 angstroms is obtained. Such films are valuable for use in printed and integral electronic circuitry applications. Of course the film thickness obtainable is limited by the amount of penetration of the titanium by diffusion during the titanium deposition process and homogeneous copper-titanium films of at least 25,000 angstroms can be formed by this method. It is to be noted that titanium deposition methods such as disclosed in the previously mentioned patents can also be used for the titanium deposition step of forming this copper-titanium alloy film, but as explained previously, the simplified sandwich titanium deposition method described herein is much more advantageous from the viewpoint of simplicity, expense and suitability for semi-automatic and/or mass production techniques.

It is to be understood that the description of the present invention contained herein is only exemplary and that many variations are possible. It will be appreciated that the present invention may be applied to any type of arrangement for coating titanium, zirconium, hafnium or uranium in which a sandwich assembly such as disclosed herein may be employed. The present invention, therefore, is to be considered as including all possible modifications and variations coming within the scope of the invention as defined in the appended claims.

We claim as our invention:

1. A method of forming a metal coating on the surface of a body which comprises sandwiching a thin layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a layer of coating metal from the group consisting of titanium, zirconium, hafnium and uranium and the surface to be coated, and then heating the resultant sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit a coating of metal on the surface of said body, the thickness of the layer of salt being sufficient to provide a liquid boundary between said layer of metal and the surface to be coated when the salt melts.

2. A method of forming a titanium coating on the surface of a body which comprises sandwiching a thin layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a layer of metal containing titanium and the surface to be coated, and then heating in an air environment the resultant sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit a titanium coating on the surface of said body, the thickness of the layer of salt being sufficient to provide a liquid boundary between said layer of metal and the surface to be coated when the salt melts.

3. A method of forming a titanium coating on a flat surface of a body which comprises sandwiching a thin layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a layer of metal containing titanium and the surface to be coated, and then heating in an air environment the resultant sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit a titanium coating on the surface of said body, the thickness of the layer of salt being sufficient to provide a liquid boundary between said layer of metal and the surface to be coated when the salt melts.

4. A method of forming a titanium coating on a flat metal surface of a body which comprises sandwiching a thin layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a layer of metal containing titanium and the surface to be coated, and then heating in an air environment the resultant sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit a titanium coating on the surface of said body, the thickness of the layer of salt being sufficient to provide a liquid boundary between said layer of metal and the surface to be coated when the salt melts.

5. A method of forming a titanium coating on the flat surface of a substrate which comprises sandwiching a thin layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a layer of metal containing titanium and the surface to be coated, and then heating in an air environment the resultant sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit a titanium coating on the surface of said body, the thickness of the layer of salt being sufficient to provide a liquid boundary between said layer of metal and the surface to be coated when the salt melts.

6. A method of forming a titanium coating on the flat surface of a substrate which comprises sandwiching a thin layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a layer of metal containing titanium and the surface to be coated, heating in an air environment the resultant sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit a titanium coating on the surface of said body, the thickness of the layer of salt being sufficient to provide a liquid boundary between said layer of metal and the surface to be coated when the salt melts, allowing the sandwich assembly to cool, separating the substrate from the sandwich, and then washing off salt from the surface of the substrate.

7. A method of forming a titanium coating on a flat surface of a refractory substrate which comprises uniformly spreading a finely powdered salt on a layer of metal containing titanium until the salt is observed to cover the metal over an area at least equal to the surface area of the substrate to be coated, said salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides, placing the substrate so that the layer of salt so formed is sandwiched between the surface to be coated and the layer of metal containing titanium, heating in an air environment the resultant sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit a titanium coating on the surface of the substrate while supporting the sandwich assembly so that the salt layer is held substantially horizontal, the thickness of the layer of salt being sufficient to provide a liquid boundary between the layer of metal containing titanium and the surface to be coated when the salt melts, the layer of salt being sufficiently thin to prevent excessive running thereof, allowing the sandwich assembly to cool, separating the substrate from the sandwich, and then washing off the salt from the substrate.

8. The invention in accordance with claim 7, wherein said salt is a mixture of NaCl, KCl and KI.

9. A method of simultaneously forming titanium coatings on opposite surfaces of a substrate and on the interior surfaces of apertures and cavities therein which comprises forming a five-layer sandwich assembly made up of a first layer of metal containing titanium, a first thin layer of salt, the substrate, a second thin layer of salt and a second layer of metal containing titanium in that order, the salt making up said layers of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides, and then heating the sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit titanium coatings on said opposite surfaces of the substrate, the thicknesses of the first and second salt layers being sufficient to provide liquid boundaries between said opposite surfaces of the substrate and the first and second layers of metal containing titanium when the salt melts.

10. A method of simultaneously forming titanium coatings on opposite surfaces of a substrate and on the interior surfaces of apertures and cavities therein which comprises forming a five-layer sandwich assembly made up of a first layer of metal containing titanium, a first thin layer of salt, the substrate, a second thin layer of salt and a second layer of metal containing titanium in that order, the salt making up said layers of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides, then heating in an air environment the sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit titanium coatings on said opposite surfaces of the substrate, the thicknesses of the first and second salt layers being sufficient to provide liquid boundaries between said opposite surfaces of the substrate and the first and second layers of metal containing titanium when the salt melts, allowing the sandwich as-

sembly to cool, separating the substrate from the sandwich, and then washing off salt from the substrate.

11. A method of forming a thin film of a copper-titanium alloy on the surface of a body which comprises first coating said body with a thin copper film, then sandwiching a thin layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a layer of metal containing titanium and the copper-coated surface of said body, and then heating the resultant sandwich assembly to a temperature and for a time sufficient to convert the copper film into a copper-titanium alloy film, the thickness of the layer of salt being sufficient to provide a liquid boundary between said layer of metal and the copper-coated surface of said body when the salt melts.

12. A method of forming a thin film of a copper-titanium alloy on the surface of a refractory body which comprises first coating said body with a thin copper film of less than 10,000 angstroms, then sandwiching a thin layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a layer of metal containing titanium and the copper-coated surface of said body, and then heating the resultant sandwich assembly to a temperature and for a time sufficient to convert the copper film into a copper-titanium alloy film, the thickness of the layer of salt being sufficient to provide a liquid boundary between said layer of metal and the copper-coated surface of said body when the salt melts.

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