July 4, 1961 R. A. QUINN 2,991,195

METHOD OF METALLIZING HOLES AND CAVITIES WITH A REFRACTORY METAL

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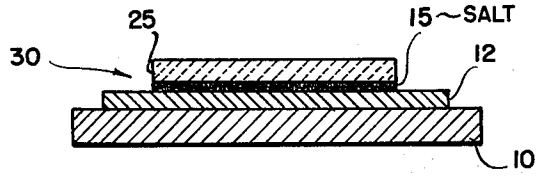


Fig. 1

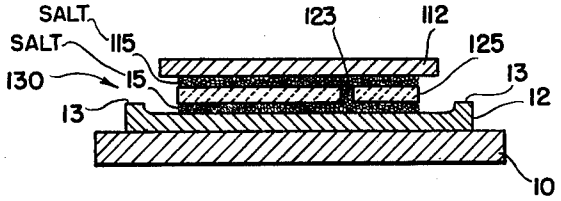


Fig. 2

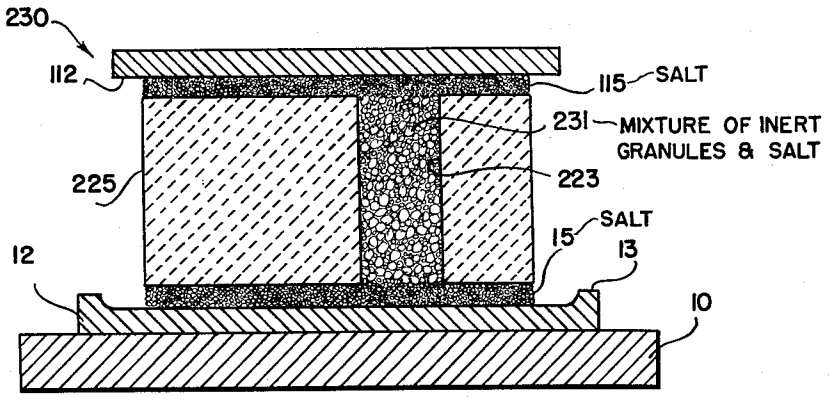


Fig. 3

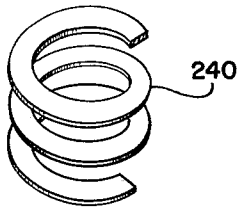


Fig. 4

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METHOD OF METALLIZING HOLES AND CAVITIES WITH A REFRACTORY METAL

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8 Claims. (Cl. 117—120)

This invention relates generally to methods of coating a body with a refractory metal, and more particularly to a simplified method by means of which holes and cavities of considerable depth within a body can be uniformly coated with a refractory metal.

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 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 would thereby limit any practical use of either of these coating methods for printed or integrated electronic circuit applications.

In copending patent application Serial No. 8,157 a highly simplified method is disclosed which permits a body to be coated with titanium or the related metals of zirconium, hafnium or uranium without the need for a bath into which the body to be coated must be immersed as in the aforementioned patents. Because of its convenience and simplicity, this method has been found to be well suited for semi-automatic and/or mass production techniques.

The method disclosed in this copending patent application derives its simplicity and convenience as a result of the use of a sandwich assembly in which a thin layer of salt essentially consisting of at least one chosen from

the group consisting of the alkali and alkaline earth metal halides is sandwiched between the surface of the body to be coated and a layer containing the coating metal, such as titanium. Contrary to what might be expected from previous concern with the problem of oxidation, 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 or any of the other previously mentioned related metals can be successfully deposited on the body without the occurrence of deleterious amounts of oxidation. This highly advantageous result is obtained because when the salt layer melts it forms a liquid boundary between the surface being coated and the layer of coating metal which serves as a sufficient barrier to prevent oxidation from deleteriously interfering with the deposition process. Below the temperature at which the salt melts, some air is introduced into the system but causes no problem because the salt melts at a sufficiently low temperature to prevent any deleterious oxidation of the titanium surface from taking place.

Using the method disclosed in the aforementioned copending patent application, it was found that holes and cavities of reasonable depth in the body are also coated with a film of coating metal during the process as a result of melted salt flowing along the sides of the hole or cavity. The ability to coat holes or cavities in this manner has been found to offer very significant advantages in printed and integrated circuitry applications and for this reason improved techniques for coating such holes and cavities, particularly those of considerable depth, has taken on new importance.

It has been found that the method disclosed in the aforementioned copending patent application does not successfully coat holes and cavities of any considerable depth (greater than about ½ inch), even if the hole is filled with salt prior to heating. As a result, it has been necessary to use unwieldly bath-immersion techniques, such as disclosed in the two previously mentioned patents, in order to successfully coat deep holes and cavities and this has significantly limited practical development of integrated circuitry.

The main object of the present invention is to improve on the method of the aforementioned copending patent application so that the simplified and convenient sandwich assembly technique disclosed therein is also capable of successfully and reliably coating deep holes and cavities with a uniform thin film of coating metal, which may be titanium, zirconium, hafnium or uranium, the metal of primary interest being titanium.

Another object of this invention is to provide a simplified method for simultaneously forming a thin uniform film of titanium on one or both sides of a refractory substrate, and also on the interior surfaces of one or more deep holes or cavities in the substrate.

An additional object of this invention is to provide a new and simple method for forming a thin alloy film on one or more surfaces of a body, and also on the interior surfaces of large holes and cavities therein.

In a typical embodiment of the invention, the above objects are accomplished by first providing a sandwich assembly as disclosed in the aforementioned copending patent application, then loosely packing deep holes or cavities in the substrate with granules of an inert solid material such as alumina which will remain solid during the deposition process, and then pouring into the hole a salt mixture essentially consisting of one or more of the alkali or alkaline earth metal halides. The granules packed into the hole or cavity are made of sufficient size so that during the deposition process when the salt is molten, the surface tension of the molten salt with respect to the area of the granules acts to hold the molten salt in the hole or cavity so as to effectively wet the entire inner surface of the hole

and permit a uniform thin film to be deposited thereon along with the other surfaces of the sandwich assembly. For films of very high uniformity it has been found advantageous to initially place a thin spiral of the coating metal in the hole or cavity before packing with the granules of inert material and pouring in the salt. Such a thin spiral of coating metal contributes to the uniformity of the coating obtained by providing a source of titanium in close proximity to the interior surfaces of the hole or cavity.

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:

FIGS. 1 and 2 are cross-sectional views of sandwich assemblies which may be employed in practicing the method disclosed in the aforementioned copending patent application.

FIG. 3 is a cross-sectional view of a sandwich assembly showing in detail how a hole through a thick substrate may be filled with granules of an inert solid material and the alkali or alkaline earth metal salt mixture to permit the hole to be uniformly coated along with the other surfaces of the body.

FIG. 4 is a perspective view of a thin spiral of the coating metal which may be additionally provided in the hole of the assembly of FIG. 3 for the purpose of obtaining a highly uniform coating on the interior surfaces thereof.

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

In order to provide a better understanding of the present invention, the method disclosed in the aforementioned copending patent application will be described in detail using FIGS. 1 and 2.

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 of 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.

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.

It has been discovered that when the assembly **30** is heated the melted salt itself serves 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. Because the surface tension of the molten salt tends 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 assembly is vertical some means must be provided for holding the sandwich together during heating.

In actual practice satisfactory titanium deposition has been accomplished using thin layers of titanium and alumina substrate from about .010 inch to 1 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 the 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.

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, and also permits the interior surface of a hole or aperture **123** of reasonable depth in the substrate **125** to be coated with a uniform film of substantially the same thickness. 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 allow 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. For holes of small depth it has not been found necessary to fill the hole with salt in order to obtain a satisfactory coating on the interior surface thereof. As the hole becomes deeper, however, filling it with salt does permit deeper holes up to ½ inch to be satisfactorily coated.

When the five layer sandwich assembly **130** of FIG. 2 is subjected to heating, both surfaces of the substrate **125** will be coated with titanium of substantially the same thickness since both are subject to the same temperature for the same time. Also, if the hole **123** in the substrate **125** is not too deep, the interior surface thereof will also be coated with a titanium film of the same thickness. 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.

Using the sandwich assembly **130** of FIG. 2 it has been found impossible to obtain satisfactory coatings on the interior surfaces of holes greater than ½ inch in depth, even if the hole is relatively tightly packed with salt. This is because when the salt melts it runs out the bottom of the hole, and if the hole is deep, some portions of the interior surface especially at the middle of the hole, will have insufficient salt to permit a satisfactory coating to be deposited thereon.

In order to permit the sandwich assembly **130** of FIG. 2 to be successfully employed for coating holes or cavities in a substrate which may be as deep as four inches in some cases, the improvement of the present invention is provided which will be described in connection with FIGS. 3 and 4.

In FIG. 3 a sandwich assembly **230** is provided which

is basically similar to that of the sandwich assembly **130** of FIG. 2, except that the substrates **225** is very much thicker than the substrate **125** of FIG. 2 and the hole **223** therein is considerably deeper. In accordance with the present invention, the hole **223** in the substrate **225** is filled with material indicated at **231** which essentially comprises a mixture of a salt which is preferably the same as that of the layers **15** and **115**, and granules of a solid inert material such as alumina which remain solid at the elevated temperatures to which the assembly **230** is heated. Granules of refractory material such as boron nitride, lava and steatite may also be used. The larger size particles in the mixture **231** in the hole **223** indicate these granules of inert material while the small size particles indicate the salt. The size of the granules of inert material and the number of such granules in the mixture **231** are chosen for the particular size hole **223** so that when the salt melts, the granules of inert material remain solid and loosely packed in the hole **223** and the surface tension of the molten salt with respect to the surface area of the granules tends to hold the molten salt in the hole **223** and effectively wets the entire inner surface thereof. In actual practice experience has shown that deep holes can be satisfactorily coated using a mixture **231** obtained by first loosely packing in the hole **223** granules of inert material of the order of $\frac{1}{32}$ inch and then pouring the salt into the hole **223** until it is essentially filled.

Where highly accurate uniformity of the film coating is important, it has been found additionally advantageous to provide in the hole **223** a thin spiral of the coating metal (which may conveniently be a lathe cutting) which is somewhat smaller than the depth of the hole **223**, such as illustrated in FIG. 4 at **240**. In such a case the spiral **240** may first be placed in the empty hole **223**, the inert solid material granules loosely packed in the hole, and then the salt poured into the hole **223** until it is just about filled. The provision of such a spiral of the coating metal **240** is able to achieve a much more uniform coating because it provides a source of the coating metal in relatively close proximity to all portions of the interior surface of the hole **223**.

After the sandwich assembly **230** is heated to the temperature and for the time required to deposit a desired thickness of coating metal on the surfaces of the substrate **225** and on the interior surface of the hole **223**, the assembly **230** is cooled, separated and the substrate washed to remove the granules of inert material and the titanium spiral in the hole **223** and any adherent salt on the substrate **225**.

It is to be understood in conection with the present invention that various other types of deep holes and cavities may be uniformly coated in accordance with the invention. For example, an arrangement could be employed using a thick substrate in a 3-element assembly such as shown in FIG. 1 or in an arrangement where the hole did not go completely through the substrate. The arrangement of FIG. 3 is used for illustrative purposes because this is the main way in which the invention has been employed in practice where both sides of a substrate and the interior surface of a deep hole therein are to be uniformly coated with a thin film of coating metal.

The following specific example of the present invention will now be provided, and it is to be understood that this specific example is in no way intended to limit the scope of the invention. Referring now to FIG. 3, the salt layers **15** and **115** and the salt within the holes **223** are a salt mixture essentially consisting of 22 mole-percent NaCl, 53 mole-percent KCl, and 25 mole-percent KI. This salt mixture is obtained by grinding these constituents in a mortar and pestle to a fine intermittently mixed powder which is dried for at least twenty-four hours before use at 100° centigrade in a vacuum oven. First, the powder is 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** corresponding to the lower surface of the substrate **225** which is to be coated with titanium.

The substrate **225** having a large size hole **223** therein is now rested on the salt layer **15**. A thin spiral of titanium such as illustrated by **240** in FIG. 4 is then dropped in the hole **223** in a manner so that it retains its essential spiral shape. Preferably the diameter of the spiral **240** is of the same order as the diameter of the hole **223** so as to be held substantially upright therein. The hole **223** is now loosely packed with granules of alumina having a diameter of the order of $\frac{1}{32}$ inch until the hole **223** appears substantially filled with these granules. The NaCl-KCl-KI salt mixture is then poured into the hole **223** until it is substantially filled.

The second salt layer **115** is now provided in the same manner as the salt layer **15** by spreading it uniformly through a fine mesh screen until the salt powder appears to just cover the upper surface of the substrate **225**. The top layer of titanium **112** is then rested on the salt layer **115** and the resultant assembly **230** heated for the temperature and time required to deposit a titanium coating of the desired thickness on the upper and lower surfaces of the substrate **225** and on the interior surface of the hole **223**.

I have found that using the above described method of the present invention for coating the interior of large diameter and large depth holes, I have been able to successfully provide uniform coatings on the interior surfaces of holes as deep as four inches and even this does not seem to be the limit which can successfully be coated by the method of the present invention.

In choosing the granules of inert solid material for use in the hole **223**, it has been found that neither the quantity nor the size of the granules used are critical and a wide latitude is possible in the choice thereof. The important requirement is that the granules remain loosely packed in the hole when the salt melts and provide a sufficient area so that the surface tension of the molten salt with respect to the surface area of the granules tends to hold the molten salt in the hole and effectively wets the entire surface thereof. Ordinarily, therefore, the granules of inert material fill the greater part of the volume in the hole. Also, when using the spiral of titanium **240** in order to obtain highly uniform coatings, the particular shape or form of the titanium is not critical, the important feature being to provide a source of titanium in relatively close proximity to all portions of the interior surface of the hole during the depositition process.

As mentioned initially the simplified sandwich assembly coating technique of the aforementioned copending patent application can be employed for a wide range of applications. This is also true of the improved method of the present invention which permits deep holes to be successfully coated using the basic simplified sandwich assembly technique. It is possible, therefore, to employ the method of the present invention for forming a thin alloy film on the interior surfaces of deep holes in the same way that a thin alloy is formed on a surface as disclosed in the aforementioned copending patent application.

In this method of the aforementioned copending patent application, a body is first coated with a thin film of metal by any well known method, such as vacuum evaporation. The metal coated body is then subjected to the sandwich assembly deposition treatment using the basic sandwich assembly technique described in the aforementioned patent application. During this treatment, alloying and deposition occur simultaneously so that the final surface film obtained is not a layer of the coating metal, but is an alloy of both metals. For example, if copper is first coated on a body and titanium used as the coating metal, a surface film is obtained which is not a layer of titanium but is an alloy of copper and titanium, the percentage

composition being dependent upon the thickness of the copper and the length of time of the titanium deposition.

In the present invention, deep holes of a substrate are provided with a thin alloy film by first coating the hole with a thin layer of metal and then subjecting the thick substrate to the metal deposition treatment described in connection with FIG. 3 where granules of an inert material are provided in the hole. An example of such a process involves coating a thick refractory substrate and the interior surfaces of any deep holes therein with a thin film of copper of the order of 10,000 angstroms. The body and the deep holes are then subjected to a titanium deposition process as described in connection with FIG. 3 using alumina as the granular material until a total thickness of 20,000 angstroms is obtained. The resultant alloy film thereby obtained on the surfaces of the body and the interior surfaces of any deep holes will be a 50–50 percent alloy of copper and titanium.

It is to be understood that the description of the invention contained herein and the illustrative examples given are only exemplary and that various modifications in construction and arrangement are possible. 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.

I claim as my invention:

1. A method of forming a metal coating on a surface of a body and the interior surfaces of a deep hole therein which comprises essentially filling the hole with a mixture of granules of an inert solid material and a salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides, sandwiching a thin layer of salt chosen from the same group as the salt in the hole 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 and the interior surface of each deep hole and cavity, 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, the size and quantity of the granules of inert material making up the mixture in the hole being chosen so that the granules remain solid and loosely packed in the hole at the temperature to which the assembly is heated and provide a sufficient area so that the surface tension of the molten salt with respect to the surface area of the granules tends to hold the molten salt in the hole and effectively wets the entire surface thereof.

2. The invention in accordance with claim 1, wherein the additional step is provided of inserting a piece of said coating metal into the hole prior to filling the hole with said mixture of granules and salt.

3. The invention in accordance with claim 2, wherein said coating metal is titanium, and said body is a refractory substrate.

4. A method of simultaneously forming titanium coatings on opposite surfaces of a substrate and on the interior surface of a deep hole therein which comprises sandwiching a first layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a first layer of metal containing titanium and one of the opposite surfaces of said substrate, filling the deep hole in said substrate with a mixture of granules of an inert solid material and a salt chosen from the same group as said first layer of salt, the greater volume of said hole being filled with the granules of inert material, sandwiching a second layer of salt from the same group as said first layer of salt between a second layer of metal containing titanium and the other of the opposite surfaces of said substrate, and then heating in an air environment the resultant five-layer sandwich assembly to a temperature and for a time sufficient to melt the salt and deposit a coating of titanium on the opposite surfaces of said substrate and on the interior surface of the deep hole, the thickness of the layers of salt being sufficient to provide a liquid boundary between each of the opposite surfaces of the substrate and its respective layer of metal containing titanium, the size of the granules of inert material making up the mixture in the hole being chosen so that the granules remain solid and loosely packed in the hole at the temperature to which the assembly is heated and provide a sufficient area so that the surface tension of the molten salt with respect to the surface area of the granules tends to hold the molten salt in the hole and effectively wets the entire surface thereof.

5. The invention in accordance with claim 4 wherein the additional step is provided of inserting into the hole a thin spiral of metal containing titanium prior to filling the hole with said mixture of granules and salt.

6. The invention in accordance with claim 5 wherein the additional steps of allowing the sandwich assembly to cool, separating the substrate from the sandwich, and washing the substrate are provided after said heating.

7. A method of simultaneously forming a thin alloy film on opposite surfaces of a refractory substrate and on the interior surface of a deep hole therein which comprises first coating the opposite surfaces of the substrate and the interior surface of the hole with a thin film of copper, then sandwiching a first layer of salt consisting essentially of at least one chosen from the group consisting of the alkali and alkaline earth metal halides between a first layer of coating metal from the group consisting of titanium, zirconium, hafnium and uranium and one of the opposite surfaces of said substrate, filling the deep hole in said substrate with a mixture of granules of an inert solid material and a salt chosen from the same group as said first layer of salt, the greater volume of said hole being filled with the granules of inert material, sandwiching a second layer of salt from the same group as said first layer of salt between a second layer of said coating metal and the other of the opposite surfaces of said substrate, and then heating in an air environment the resultant sandwich assembly to a temperature and for a time sufficient to convert the copper film into an alloy of copper and said coating metal, the thickness of the layers of salt being sufficient to provide a liquid boundary between each of the opposite surfaces of the substrate and its respective layer of coating metal, the size of the granules of inert material making up the mixture in the hole being chosen so that the granules remain solid and loosely packed in the hole at the temperature to which the assembly is heated and provide a sufficient area so that the surface tension of the molten salt with respect to the surface area of the granules tends to hold the molten salt in the hole and effectively wets the entire surface thereof.

8. The invention in accordance with claim 7 wherein said coating metal is titanium and the copper film coated on the substrate has a thickness of less than 10,000 angstroms.

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