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COATING REFRACTORY METALS

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FIG. 1.

*SURFACE OF SLAB OF METAL OF THE GROUP
CONSISTING OF MOLYBDENUM, TUNGSTEN
AND ALLOYS IS CLEANED.*

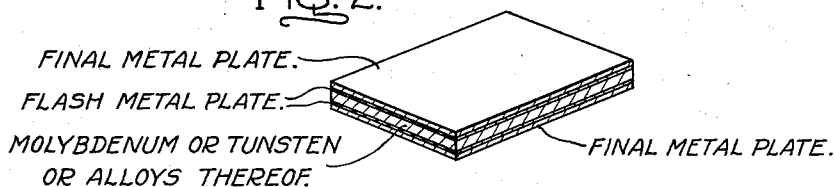
*CLEANED SLAB PROVIDED WITH FLASH
PLATE OF METAL OF THE GROUP CONSISTING
OF COPPER, SILVER AND GOLD.*

*FLASH PLATED SLAB HEAT TREATED IN
REDUCING ATMOSPHERE TO MELT FLASH PLATE
FOR A TIME SUFFICIENT TO FREE SLAB
FROM ALL GASEOUS MATERIAL AND OXIDES.*

*FINAL PLATE OF METAL OF THE GROUP
CONSISTING OF NICKEL, COPPER, SILVER
AND GOLD ELECTRODEPOSITED ON FLASH
PLATE FROM ELECTROLYTIC SOLUTION
CONTAINING SOLVENT FOR OXIDE OF
METAL OF FLASH PLATE.*

*FLASH PLATE AND FINAL PLATE BONDED
TO SLAB BY HOT ROLLING REDUCTION
OF SLAB TO DESIRED THICKNESS.*

FIG. 2.



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COATING REFRACTORY METALS

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The present invention relates to composite metal bodies and more particularly to such bodies including a base of molybdenum, or tungsten, or alloys of these metals having thereon a thin coating of less refractory metal, such as nickel, copper, silver and gold.

In silicon semiconductor rectifiers it is desirable to solder the silicon crystal, which is in the form of a wafer, to a molybdenum member which may constitute the base member or the separator plate of the rectifier. Soldering the silicon wafer directly to the molybdenum has not been found practical in many rectifier types and it has been proposed to coat the molybdenum member with a metal that the solder will wet. Nickel, silver and gold are suitable coating metals but difficulty has been encountered in applying an adherent nickel coating on molybdenum. Nickel does not adhere well to molybdenum especially when the coated member is subjected to elevated temperatures. High melting point solders, that is, solders having a melting temperature of approximately 620° C. to 1100° C., are used for soldering silicon wafers to the molybdenum member. Coatings of nickel tend to separate from the molybdenum when such solders are used.

In soldering the molybdenum member to its mount in such rectifiers a copper coating on the molybdenum member is often desirable.

The principal object of the present invention is to provide a composite metal body including a molybdenum base and a metal coating thereon to which body a silicon wafer may be soldered or brazed.

Another object of the invention is to provide composite metal articles having a refractory metal base of molybdenum, tungsten, molybdenum base alloys, or tungsten base alloys and an adherent coating of nickel, copper, silver, or gold firmly bonded to the refractory metal base and free from blistering, flaking or peeling during fabrication and use of the article at elevated temperatures and a method of producing such articles.

Further objects and advantages of the invention will become apparent from the following disclosure.

Referring to the drawing:

FIG. 1 is a flow diagram illustrating how the present invention may be practiced, and

FIG. 2 is a perspective fragmentary view of a product in accordance with the present invention.

As an example of the invention, the best mode contemplated for carrying out the method of the invention is described in the following disclosure of steps effective for applying an adherent metal coating to a molybdenum base.

The method comprises the steps of rolling a molybdenum ingot to form a slab of a size suitable for electroplating and to a thickness which can be reduced by further rolling to a temperature below the melting temperature of the metal or metals constituting the coating on the finished article. The molybdenum slab is caustic cleaned and acid washed after rolling to remove all oxides and contaminants.

A strike or flash metal plate or layer and then a final metal plate or layer are applied to the cleaned molybdenum slab by electrodeposition. The flash layer, which may be 0.0001" to 0.0005" thick, consists of the metal forming the final layer or of a different metal which is compatible with both the molybdenum and the metal of the final layer. By a compatible metal is meant one

which does not form a brittle alloy with molybdenum or with the metal of the final layer but one which, when heated above its melting point in a reducing atmosphere, will wet the molybdenum and will also serve as a suitable substrate, when solid, for further plating with the desired metal of the final layer. For example, a flash layer of copper, silver, or gold is suitable for applying a final layer of nickel to the molybdenum slab. When the final metal layer is of copper, silver or gold the flash layer may consist of the same metal as the final layer or any metal of the group consisting of these metals.

After the flash layer has been electroplated on the molybdenum slab and before the final layer is electroplated on the flash layer, the plated slab is heat treated in a reducing atmosphere, preferably dry hydrogen, by raising its temperature above the melting point of the metal of the flash layer and maintaining it at such temperature in such atmosphere with the flash layer in molten condition for the time required to free the surface of the molybdenum slab and the flash layer from all gaseous material and oxides. This is of critical importance to the success of the method as explained below.

Before the flash coated molybdenum slab is removed from the reducing atmosphere and exposed to an oxygen containing atmosphere, such as air, the temperature of the coated slab is reduced to solidify the molten metal of the flash layer on the surface of the slab so that the flash layer in its solidified state protects the molybdenum from oxidation.

The exposed surface of the flash layer oxidizes almost immediately on exposure to air and it then becomes necessary to free the flash layer from its oxides. For this purpose the bath used in electroplating the metal of the final layer is of such nature that the oxide or oxides of the metal of the flash layer are soluble therein. In this manner all oxides and gaseous materials are removed from both the molybdenum surface and the surface of the flash layer on the slab before plating with the metal of the final layer begins. This is also of critical importance to the successful carrying out of the method.

In order for the molybdenum to remain covered by the flash layer it is necessary that the metal of this layer does not alloy with or dissolve in the molybdenum when molten. Silver, copper and gold fulfill this requirement. Nickel, however, does not because a flash layer of nickel when molten is soluble in and diffuses into the surface of the molybdenum slab forming nickel molybdenum alloy on the surface of the slab. The nickel molybdenum alloy forms complex molybdenum nickel oxides which are not soluble in the plating bath used for electroplating the metal of the final layer. These complex oxides remain trapped under the final layer and are reduced on subsequent annealing of the coated molybdenum in a reducing atmosphere, such as dry hydrogen, and give off gas causing blisters in the final layer.

In accordance with the present invention, a final layer of nickel is electroplated on a flash layer of different metal, preferably a copper flash layer, on a molybdenum slab to produce a nickel plated molybdenum slab suitable for further processing as follows.

After the final plating, the coated molybdenum slab is heated to a temperature suitable for hot rolling reduction of the slab to sheet thickness but below the temperature which would result in melting of the metal in the final layer of the coating. In the case of a final layer of nickel on a flash layer of copper, for example, the rolling temperature may be such that, during the rolling, copper of the flash layer dissolves in the nickel of the final layer forming a thin nickel copper alloy layer under the nickel final layer which is firmly bonded to the molybdenum. The heating time and the temperature of the slab are carefully controlled during each pass of the slab through

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the rolls. This is of particular importance in the case of a final layer of nickel to prevent diffusion of the nickel into the molybdenum causing formation of a brittle interface. As a result of the rolling under the conditions disclosed below the final metal layer is attached to the molybdenum sheet by mechanical bonding and welding and there is no solution of the coating metal or metals, or metal alloys, or diffusion of the coating metal or metals in the molybdenum part of the final product. After completion of the rolling the coated sheet is annealed in a reducing atmosphere.

Discs, squares, or articles of other shapes may be stamped, or punched from the molybdenum sheet coated with nickel, copper, silver, or gold and wafers cut from silicon crystals may be soldered to the articles having a final layer of nickel, silver or gold by high melting point solders without causing the coating to flake, peel or blister.

An example of a method illustrating features of the invention is the following. A standard molybdenum ingot 1" thick, 5" wide and 6" long is rolled until it is approximately 0.250" thick, 5" wide and 24" long. The molybdenum slab thus produced is caustic cleaned and acid washed to remove all oxides and contaminants. Immersion in a molten caustic, such as molten potassium or sodium nitrite, followed by an acid wash in a solution of $\frac{1}{3}$ nitric acid, $\frac{1}{3}$ sulphuric acid and $\frac{1}{3}$ water, for example, is effective for this purpose.

The clean slab is coated with a flash layer of copper by electrochemical deposition. The flash layer is approximately 0.0001" thick and is electroplated on the slab from an electrolytic aqueous solution containing about 30 grams per liter sodium cyanide, 22 grams per liter copper cyanide, 15 grams per liter sodium carbonate and $\frac{1}{2}$ gram per liter sodium thiosulphate. The temperature of the solution during plating is approximately 140° F. and the current density is approximately 25 amperes per square foot at 6 volts. The time required for producing a copper flash layer of the above thickness is approximately 30 seconds. The flash plated molybdenum slab is removed from the plating bath and cleaned by rinsing in water.

The plated and rinsed slab is then placed in a furnace containing a dry hydrogen atmosphere and is heated to a temperature of 1100° C. to 1200° C., inclusive, for 30 minutes to one hour. This heat treatment melts the flash layer of copper which forms a molten layer completely covering the molybdenum. The time is sufficient for all gaseous materials on the surface of the molybdenum to be boiled off and for the hydrogen to diffuse through the molten copper flash layer and reduce any oxide of molybdenum present. The molten flash layer of copper does not ball up or boil off and as all the gases and reduction products from the molybdenum come off at a time when the flash layer of copper is liquid no permanent blisters or imperfections remain in the copper flash layer after the reactions have taken place.

The temperature to which the copper flash layer is heated may be any temperature above the melting point of copper, such as a temperature of 1100° C. as specified above, and below the temperature at which the copper boils off the molybdenum. Heating above a temperature of 1400° C. will cause the copper flash layer to boil and, therefore, should be avoided. Regardless of the temperature within these limits to which the flash layer is heated the minimum heating time required is 30 minutes for freeing the flash plated slab from all oxides and contaminants which would cause imperfections in the final product. Increasing the temperature from 1100° C. to 1300° C. for example, does not reduce the minimum heating time of 30 minutes required for assuring success of the method.

Further, a neutral atmosphere, such as nitrogen, is not effective for reducing the oxides and for freeing the flash plated slab from all matter which would cause an imperfect product to be produced.

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After the flash plated slab has been heated for at least 30 minutes at the required temperature it is moved into the cooling chamber of the furnace which chamber also contains a dry hydrogen atmosphere in which the copper flash layer solidifies. It is of critical importance that the coated hot slab be protected from an oxidizing atmosphere at all times until the copper flash layer has solidified so that there is no possibility for the molybdenum to again become oxidized.

As is pointed out above, when the copper coated molybdenum slab is withdrawn from the cooling chamber of the furnace and the copper flash layer is exposed to air, a very light oxide coating is almost immediately formed on the flash layer. It then becomes necessary to remove all the copper oxide.

In accordance with the present invention this is accomplished by using a nickel sulfamate plating bath to electroplate nickel on the surface of the copper flash layer. Copper oxide is soluble in the sulfamic acid of the nickel sulfamate plating bath. The final nickel layer of the coating is electroplated on the copper flash layer from a nickel sulfamate aqueous solution having the following composition: 450 grams per liter of nickel sulfamate and 30 grams per liter of boric acid. A small amount, such as 0.375 gram per liter, of a wetting or antipitting agent may be included in the plating solution in accordance with the usual practice in the plating art, but this may be omitted, when desired. The plating solution has a pH of approximately 4, the temperature of the solution during plating is approximately 120° F. and the current density approximately 80 amperes per square foot at 2 volts. The time may be selected to produce a final layer of the desired thickness, a time of 180 minutes being effective for producing a final nickel layer 0.0061" thick on a copper flash layer 0.0001" thick to obtain a total thickness of the coating of 0.0062".

The nickel on copper plated slab is then removed from the bath and rinsed with water prior to the rolling of the slab to the desired thickness.

A rolling schedule suitable for carrying out the invention and given by way of example is the following. When the starting thickness of the molybdenum in the slab is 0.250", the starting thickness of the metal coating on the slab is 0.0062" and the desired total thickness of the final sheet is 0.040" with a coating thickness of 0.001", the molybdenum slab provided with a nickel on copper coating by the method described above is heated prior to the first pass through the rolls to a temperature of 1000° C. and is reduced approximately 30% in total thickness on the first pass. On subsequent passes the slab is reheated to this temperature before each pass and is reduced 20% in thickness on each pass after the first until a total thickness of 0.060" is reached. The heating time for the slab before the first pass and before each of the subsequent passes is approximately 5 minutes. This hot rolling reduction of the thickness of the coated slab causes copper of the flash layer to dissolve in the nickel of the final layer and form a layer of nickel copper alloy under the final nickel layer.

Before rolling the slab to the desired final thickness of 0.040" the surface thereof is cleaned by an acid wash in a dilute solution of the same composition as is used for washing the uncoated molybdenum slab and disclosed above. After the acid wash, the coated slab is annealed in a dry hydrogen atmosphere for 30 minutes at a temperature of 900° C. This treatment removes oxides from the surface of the coated slab to brighten the surface. The slab is then rolled while at a temperature of approximately 200 to 300° C. to the desired final total sheet thickness of 0.040" and is then annealed at approximately 900° C. in a dry hydrogen atmosphere for approximately 30 minutes. The thickness of the coating including the nickel final layer and the nickel-copper-alloy layer on the finished sheet is 0.001".

The coated molybdenum sheet may be stamped,

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punched, bent, or sheared or subjected to other conventional forming operations to form articles of desired shape and the coated articles thus formed may be tumbled and subjected to high temperatures, as in brazing wafers of silicon crystal thereto, without causing the coating to separate from the molybdenum, or to flake, peel or blister on the molybdenum.

The procedure described above by way of example is also useful for applying a coating of silver or copper alone to a molybdenum base. In applying a silver coating to the molybdenum slab the slab, cleaned as described above, is electroplated with silver from a cyanide solution to a thickness of approximately 0.0002" to form the flash layer. A suitable electrolytic aqueous solution is 35 grams per liter silver cyanide, 37 grams per liter potassium cyanide and 38 grams per liter potassium carbonate. Current densities of 3 to 8 amperes per square foot at a bath temperature of 20° C. using a potential of 1 or 2 volts produces a coating of the desired thickness in about 1 minute. The silver flash layer is then heat treated in the same way as the copper flash in the above example for the same purpose. The final silver layer of the coating is applied to the flash layer by using the same plating bath as is used for applying the flash layer of silver. This bath is effective for removing any silver oxide on the flash layer before the final layer of silver is applied thereto. The thickness of the final silver layer may be the same as the final nickel layer in the above example and a time of 5 hours is sufficient for applying a layer of this thickness to the flash layer.

The rolling schedule given above and the other steps in the method, such as the cleaning of the final layer and annealing of the coated sheet in a hydrogen atmosphere is effective for producing an adherent coating of silver on a molybdenum sheet.

For applying a copper coating to a molybdenum base the same procedure is followed as in the case of applying a silver coating, that is, the same copper electroplating solution is used for applying the flash layer and final layer of the copper coating. The copper flash layer is applied to the molybdenum slab in the same manner described above in connection with the production of a nickel coated slab and by using the same copper electrolytic solution. This solution is effective for removing copper oxide from the flash layer of copper. A time of 120 minutes is effective for applying the final layer of copper of the desired thickness.

A coating of gold may be applied to the molybdenum slab using a conventional cyanide electrolytic solution for applying the flash layer and the final layer of gold and a gold coated molybdenum sheet may be produced by following the steps of the method described above for producing a silver coated molybdenum sheet. A suitable electrolytic solution for applying both the gold flash layer and the gold final layer is an aqueous solution containing 1.5 troy ounces per gallon of potassium gold cyanide and 3 ounces per gallon of potassium cyanide. A current density of 10 amperes per square foot at approximately 6 volts with a solution temperature of 140° F. is effective for applying the respective flash and final gold layers of the desired thickness in the times specified above in connection with the application of the layers of silver to a molybdenum base.

By using conventional masking techniques known in the electroplating art coatings of different metals may be applied to different surfaces of the molybdenum sheet utilizing the method of the invention. For example, a molybdenum sheet may be provided with a coating of copper on one side and a coating including a final layer of nickel on the other side by electrodepositing a flash layer of copper on both sides on the slab and thereafter heat treating the copper coated slab as described above, masking one side of the heat treated copper coated slab while electrodepositing a final layer of copper or nickel on the other side, removing the mask from the masked side

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and masking the side having the final layer of metal thereon and then electrodepositing the final layer of other metal on the unmasked side of the slab. Thereafter, the coated slab with the masking material removed may be hot-rolled to sheet thickness and processed as described above in accordance with the invention to produce articles having a base of molybdenum and a copper coating on one side and a coating including a final layer of nickel on the other side.

The method described above is effective also for producing articles of molybdenum base alloys as well as tungsten and tungsten base alloys having adherent coatings of metal of the group consisting of nickel, copper, silver and gold.

The composite metal bodies or articles of the present invention are useful in the arts generally, such as in electronic receiver and power tubes, as well as in apparatus or devices incorporating semiconductors.

It is contemplated that changes may be made by those skilled in the art in the above procedures given by way of example without departing from the spirit and scope of the invention as defined in the appended claims which are intended to cover all such changes, for example, a sheet coated on one side only may be produced by masking one side of the slab during the electroplating of the flash and final layers on the other side.

Whereas the appended claims are drawn to a method of manufacturing composite metal bodies, the bodies are separately claimed in a divisional application, Serial No. 321,995, filed October 22, 1963.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of bonding metal of the group consisting of molybdenum, tungsten, molybdenum based alloys and tungsten based alloys and metal of the group consisting of nickel, copper, silver and gold to produce composite metal bodies which comprises the steps of coating a slab of metal of the first-named group with a flash layer of metal of the group consisting of copper, silver and gold by electrodeposition, heat treating the coated slab in a reducing atmosphere by raising it to a temperature high enough to cause the metal of the flash layer to melt and maintaining the coated slab at such temperature for a time not less than 30 minutes to free the coated slab from gaseous material and oxides with the flash layer in molten condition and then solidifying the flash layer before exposing the coated slab to air by lowering the temperature of the slab to a temperature lower than the melting temperature of the metal of the flash layer, electrodepositing on the flash layer from a plating bath containing a solvent for the oxide of the metal of the flash layer a final layer of metal of the group consisting of nickel, copper, silver and gold, heating the coated slab to a temperature suitable for rolling reduction but below the melting temperature of the final metal layer and then rolling the hot slab to bond the coating to the slab and reduce the thickness of the coated slab and thereafter annealing the composite metal body in a reducing atmosphere.

2. The method of bonding molybdenum and nickel to produce composite metal bodies which comprises the steps of coating a molybdenum slab with a flash layer of copper by electrodeposition, heat treating the copper coated slab in a reducing atmosphere by raising it to a temperature high enough to melt the flash layer and maintaining the slab at such temperature for a time not less than 30 minutes to free the coated slab from gaseous material and oxides with the copper flash layer in molten condition and then solidifying the flash layer before exposing the coated slab to air by lowering the temperature of the slab to a temperature lower than the melting temperature of the copper flash layer, electrodepositing on the copper flash layer from a plating bath containing a solvent for the oxide of the copper flash layer a final layer of nickel, heating the coated slab to a temperature suitable for

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rolling reduction but below the melting temperature of the nickel final layer and then rolling the hot slab to bond the coating to the slab and reduce the thickness of the coated slab and thereafter annealing the composite metal body in a reducing atmosphere.

3. The method of bonding molybdenum and nickel to produce composite metal bodies which comprises the steps of electroplating on a molybdenum slab a flash layer of copper having a thickness of 0.0001", heat treating the copper coated slab in a reducing atmosphere by raising it to a temperature of 1100° C. to 1200° C., inclusive, and maintaining it at such temperature for 30 to 60 minutes to melt the copper layer and free the surface of the molybdenum from gaseous material and oxides with the copper layer in molten condition and then solidifying the flash layer before exposing the coated slab to air by lowering the temperature of the slab to a temperature lower than the melting temperature of the copper flash layer, electrodepositing on the copper flash layer from a plating bath

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containing a solvent for copper oxide a final layer of nickel having a thickness of 0.0061", heating the coated slab to a temperature of 1000° C. and then rolling the hot slab to bond the coating to the slab and reduce the thickness of the coated slab and thereafter annealing the composite metal body in a reducing atmosphere.

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