United States Patent [19]

Haarbye

[11] **3,880,608**

[45] **Apr. 29, 1975**

[54] **ELECTRICAL CONTACT MATERIALS CONTAINING SILVER CADMIUM OXIDE**

[75] Inventor: **Fredrick O. Haarbye,** Indianapolis, Ind.

[73] Assignee: **P. R. Mallory & Co., Inc.,** Indianapolis, Ind.

[22] Filed: **Feb. 17, 1972**

[21] Appl. No.: **227,300**

Related U.S. Application Data

[60] Division of Ser. No. 17,456, March 9, 1970, Pat. No. 3,666,428, which is a continuation-in-part of Ser. No. 722,956, April 22, 1968, abandoned.

[52] **U.S. Cl.** **228/124;** 29/473.1; 29/488; 29/504

[51] **Int. Cl.** **B23k 31/02**

[58] **Field of Search** 29/472.9, 473.1, 488, 504

[56] **References Cited**

UNITED STATES PATENTS

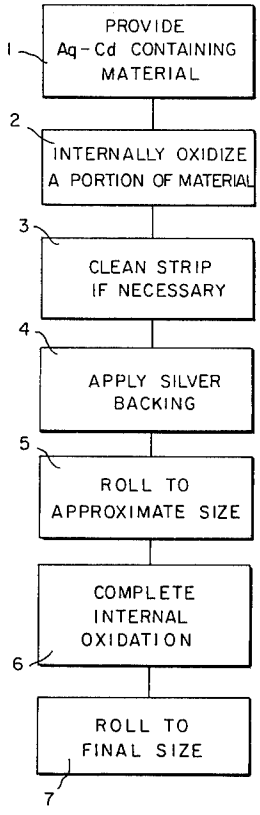
2,539,298	1/1951	Doty et al.	29/199
3,151,385	10/1964	Gwyn, Jr.	29/472.9 X
3,270,413	9/1966	Watson	29/488 UX
3,466,735	9/1969	Emmert	29/473.1 X
3,472,654	10/1969	Cowey, Jr. et al.	75/173
3,545,067	12/1970	Haarbye et al.	29/504 X
3,674,446	7/1972	Haarbye et al.	29/195
R27,075	2/1971	Murphy et al.	29/420.5

Primary Examiner—Andrew R. Juhasz
Assistant Examiner—Ronald J. Shore
Attorney, Agent, or Firm—Hoffmann Meyer & Hanson

[57] **ABSTRACT**

A silver layer is applied to a body containing a silver-cadmium alloy by first oxidizing a portion of the body, applying a bonding layer, and then the body is oxidized to the extent necessary.

11 Claims, 5 Drawing Figures



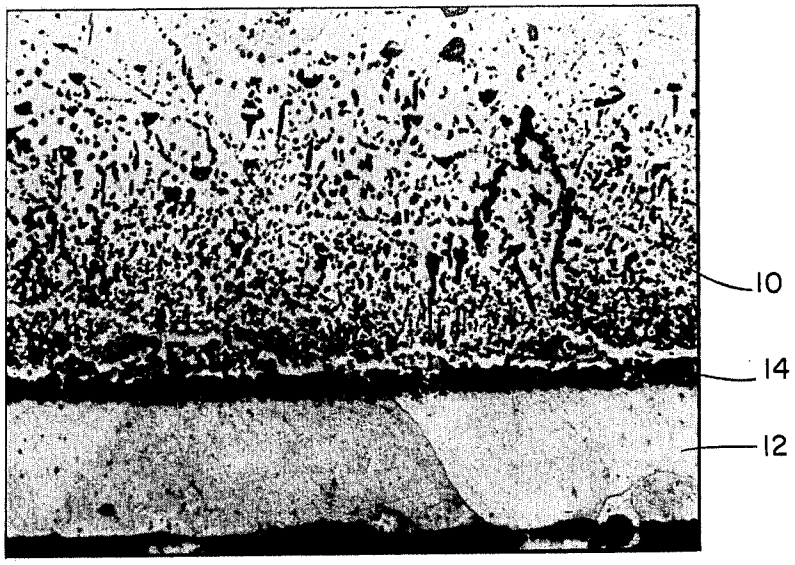


FIG. 1
PRIOR ART

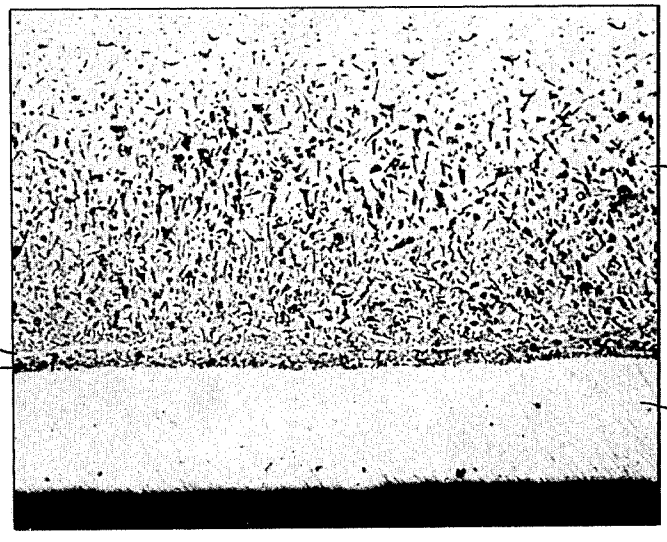


FIG. 5

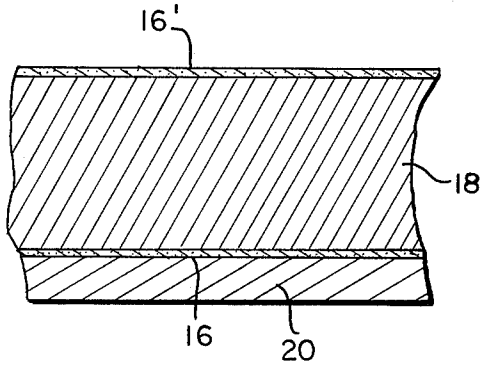


FIG. 3

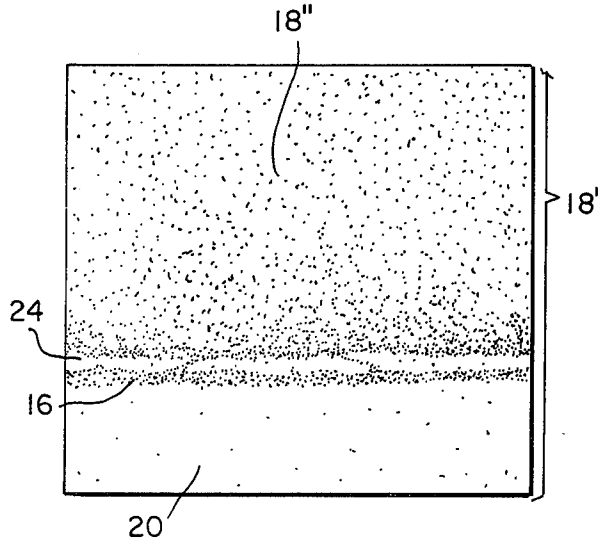


FIG. 4

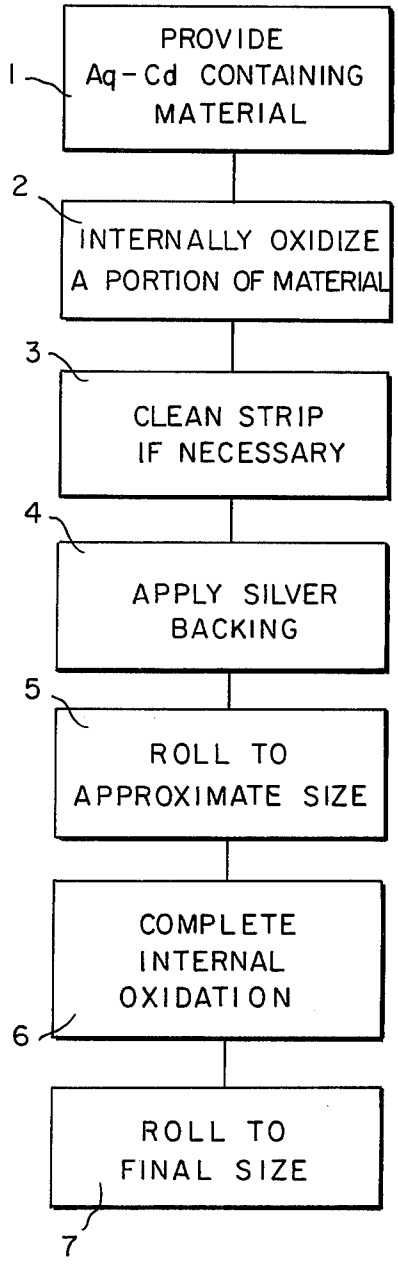


FIG. 2

ELECTRICAL CONTACT MATERIALS CONTAINING SILVER CADMIUM OXIDE

This application is a division of application Ser. No. 17,456 filed Mar. 9, 1970, now U.S. Pat. No. 3,666,428, which in turn is a continuation-in-part of application Ser. No. 722,956, filed Apr. 22, 1968, now abandoned.

Silver-cadmium oxide materials are being increasingly used as electrical contact materials in many electrical applications. Such material substantially eliminates the tendency for sticking in make and break applications and has a low resistance for better current carrying capacity. When being used as electrical contacts, the material is usually fabricated in the form of strips which are subsequently attached to a suitable backing material such as stainless steel, for example, to form the electrical contact. Such backing material forms the shank of the contact. Normally, the attachment is done by welding or brazing. However, it has been found that silver-cadmium oxide contact materials are difficult to attach directly to the stainless steel backing material through a brazing material. Silver-cadmium oxide material is, therefore, first backed with a layer of silver. Such silver backing then provides a surface to which a brazing means can be applied for attaching the silver-cadmium oxide material to the stainless steel.

In the drawings:

FIG. **1** is a photomicrograph at **300X** showing the cadmium oxide layer obtained according to prior art bonding techniques.

FIG. **2** is a block diagram showing the various steps used in carrying out the process of the present invention;

FIG. **3** is a cross-section of a silver-cadmium material showing its condition at several steps of the process;

FIG. **4** is a schematic illustration of the microstructure obtained with the process of the present invention; and

FIG. **5** is a photomicrograph at 300X of the microstructure obtained with the process of the present invention.

The application of silver backing to the silver-cadmium oxide material as described above is not, however, without its problems. For example, as shown in FIG. **1**, a heavy layer of cadmium oxide **14** is generally encountered near or at the interface of backing **12** and the main body of silver-cadmium oxide **10.** Such layer results in impairment of the attachment of the contact material to other materials such as stainless steel, because of the low mechanical strength of the cadmium oxide. Also, in applying the silver backing, it is highly desirable, because of ease of handling, that the silver be applied to a relatively thick material, about three-eights inches or more. Because of this, the silver is preferably applied to a silver-cadmium alloy rather than a silver-cadmium oxide alloy since it is difficult to reduce the thickness of silver-cadmium oxide without cracking. However, when applying the silver backing to a silver-cadmium alloy there is a strong tendency for cadmium to migrate from the main body of silver-cadmium alloy toward the surface to which the silver is being applied. Prior to attachment there is a slight gap between the backing and the unoxidized silver-cadmium alloy. Thus the above-noted cadmium oxide layer **14** is obtained.

The present invention is concerned with the method of making an electrical contact material from a body containing silver-cadmium oxide having a layer of a material which is highly thermally and electrically conductive and which is readily wettable for subsequent brazing applied thereto and has as one of its objects the provision of such a material which will not be rich in cadmium oxide at the interface between the layer and the silver-cadmium oxide containing material.

Another object of the invention is the provision of such an electrical contact wherein the layer is silver, or gold.

Another object of the invention is to provide a method of forming an electrical contact material from a body containing silver-cadmium oxide having a silver layer bonded thereto.

Another object of the invention is to provide a method of fabricating a silver-cadmium oxide containing electrical contact material with a silver layer bonded thereto wherein a barrier is established at or near the surface to which the silver layer is to be bonded.

Yet another object of the invention is to provide a method of forming a silver-cadmium oxide containing electrical contact material having a silver layer bonded thereto wherein the silver-cadmium alloy is internally oxidized at or near the surface to which the silver layer is to be applied to form the barrier.

A further object of the invention is to provide a method of forming a silver-cadmium oxide containing electrical contact material having a silver layer bonded thereto wherein the silver layer is applied after a portion of the silver-cadmium has been internally oxidized.

Still another object of the invention is to provide a method of forming a silver-cadmium oxide containing electrical contact material having a silver layer bonded thereto wherein a portion of a silver-cadmium alloy is internally oxidized prior to application of the silver layer, the silver layer applied, and the oxidation of substantially the entire material is completed.

Another object of the invention is to provide a method of making an electrical contact material comprising a silver-cadmium oxide containing body with a layer of silver bonded thereto, the body having a zone of barrier material containing silver-cadmium oxide at or near the surface of the body joined to the silver layer.

These and other objects of the invention and the nature thereof will become apparent from the following description.

Generally speaking, the objects of the invention are accomplished by providing a method of forming an electrical contact material comprising a body containing silver-cadmium oxide with at least one layer of a high electrically and thermally conductive material which is readily wettable for subsequent brazing bonded thereto, wherein the layer that is bonded to the body is applied after a portion of a silver-cadmium alloy material is first internally oxidized to form a barrier of silver-cadmium oxide, the alloy being oxidized at or near the surface of the material to which the layer is to be bonded. After the layer has been applied, the internal oxidation of the silver-cadmium containing material is then completed. The method of the invention results in an electrical contact material comprising a body containing silver and cadmium oxide having a layer of a high electrically and thermally conductive

and readily wettable material bonded to the silver-cadmium oxide containing body with substantially no massive cadmium oxide at the body layer interface.

In prior art silver-cadmium oxide contact material having a silver layer bonded thereto, there is usually a heavy deposit of cadmium oxide such as **14** in FIG. **1** at the interface between the silver layer **12** and the silver-cadmium oxide material **10.** With such a microstructure it has been found that even with the silver layer acting as a wetting means for subsequent brazing, it is very difficult to attach the silver-cadmium oxide electrical contact material to a backing material such as stainless steel. More specifically, with the heavy concentration of cadmium oxide at the braze interface when no silver layer is used, or at the interface between the silver-cadmium oxide body and the silver layer when a silver layer is used, there is obtained a bond low in strength because of the low physical strength of the cadmium oxide layer. This difficulty has been substantially eliminated by the process of the present invention.

With reference to FIGS. **2** and **3,** there is shown the particular steps used in carrying out the method of the invention. As shown, there is provided, in step **1,** a material **18** containing silver and cadmium. The material may take several forms such as sheets, wire strips, etc. Various proportions of silver and cadmium may be used in carrying out the steps of the invention. Generally speaking, in the practice of the invention there may be from 2.0 percent cadmium by weight of the total silver-cadmium containing material **18** to about 15 percent by weight, the balance being substantially silver. Exemplary percentages of cadmium by weight within this range include 2.2 percent cadmium, 4.5 percent cadmium, 9 percent cadmium, 12 percent cadmium, 13.4 percent cadmium and 15 percent cadmium, with the balance being silver. The silver-cadmium containing material is then, as shown in step **2,** internally oxidized such that a portion of the silver-cadmium is oxidized to form relatively thin zones of silver-cadmium oxide **16** and **16'**. Zones **16** and **16'** act as barriers and need to be thick enough to prevent cadmium from the balance of the material **18** from penetrating the barrier when a layer of a high thermally and electrically conductive and readily wettable material for brazing such as silver, or gold is applied to the surface. The oxidation is, in general, carried out by passing the material through a furnace in an oxidizing atmosphere such as air or pure oxygen and heating the material to a mixiumum temperature of about 850°C and preferably about 700° to about 825°C, most preferably about 800° to 825°C.

Generally speaking, the time needed to form the zone **16** is dependent upon the amount of cadmium in the material and the needed thickness of the layer. For a material having from 2–15 percent cadmium by weight, it has been found that the oxidation time may be for example from about 5 to 30 minutes depending upon temperature, preferably about 10 to 25 minutes in order to achieve a satisfactory thickness, for example of about 0.001 inch may be used. In passing the material through the furnace no particular care need be taken to assure that there will be a cadmium oxide layer only at one surface. Thus, the oxygen from the oxidizing atmosphere will penetrate all sides and ends of the material and will therefore form the other zone **16'**. The point is, however, that only a sufficient amount of oxidation occurs so as to provide a relatively thin zone **16** and **16'** to act as a barrier material.

As is next shown in step **3,** if there should be any minor amounts of cadmium oxide stain or tarnish present on the surface of the material, the material may be cleaned. Such cleaning may be done by mechanical brushing or by the use of a suitable silver cleaner such as hydrochloric acid, for example.

As is shown in step **4,** a bonding layer is then applied to the material. As previously noted, silver, gold, alloys thereof or other readily wettable material may also be used. The layer is usually applied by a hot roll bonding process. Prior to the hot rolling step, a sandwich of the material with the bonding layer is first prepared. As shown in FIG. **3,** a strip **20** for example of silver is laid over the surface to which the layer is to be applied. In order to insure adequate brazing of the silver-cadmium oxide containing material to the backing material used to form electrical contacts, the thickness of the strip **20** should be preferably from about 5–10 percent of the thickness of the silver-cadmium material **18,** a minimum of 0.005 inch at final size. This sandwich is then preheated in a furnace at a temperature of from about 700° to about 825°C for a period of about 5 to 25 minutes in an oxidizing atmosphere in order to not complete the oxidation of the silver-cadmium material. Such time, and the temperature to which the sandwich is heated, is dependent upon the rolling characteristics of the material which is partly dependent upon the amount of cadmium present. It is during the preheating step that the barrier zone **16** becomes most important. It helps to prevent migration (diffusion) of cadmium from the silver-cadmium containing material **18** to the silver-cadmium silver layer interface. Such migration will cause formation of the heavy layer of cadmium oxide at the silver layer interface, as is commonly found in prior art materials, and which is shown at **14** in FIG. **1** when the material is completely oxidized. After the sandwich has been prepared, the sandwich is fed through suitable rolling means that have been preheated to a temperature of about 300° to 450°C so as to roll and pressure weld the silver strip **20** to the material **18.** Upon passing through the roll, the thickness of the sandwich will be substantially reduced, there being about a 10–30 percent reduction with the optimum being about a 15 to 25 percent reduction in the thickness. As indicated in step **5,** the sandwich can be subsequently rolled a number of times to reduce the thickness of the sandwich to approximately the final desired size. Such rolling may be either hot rolled, or cold rolled at ambient temperatures.

As indicated in step **6** and Fig. **3,** after the rolling is completed, the silver-cadmium containing material, a portion of which has been oxidized, and having the backing layer bonded thereto is internally oxidized to complete the oxidation such that the entire silver-cadmium containing material **18** is substantially completely oxidized. Such oxidation is carried out in the manner as was done in the initial oxidation step of step **2.** The oxygen will penetrate the silver layer **20** that has been bonded to the body, but there will be substantially no penetration of cadmium from the silver-cadmium containing material **18** to the interface between the backing layer and the material **18** due to the barrier of silver-cadmium oxide **16.** The amount of time sufficient to complete the oxidation will be dependent upon the amount of cadmium present in the original silver-

cadmium containing material and the thickness of the material. As is indicated in step **7**, after the material has been completely oxidized, the material may then be rolled to final size if necessary.

With particular reference to FIGS. **4** and **5**, the final structure is shown. The structure **18'** will comprise a body containing silver-cadmium oxide **18''**, a silver layer **20** bonded to the silver-cadmium oxide containing body **18''** with substantially no massive cadmium oxide present at the interface. Additionally there will be present region **24** containing fine cadmium oxide particles, covered by a relatively thin zone **16** of silver-cadmium oxide of slightly coarser cadmium oxide particle size, unless the entire body has been oxidized in the first oxidation step, as will be the case with thin silver-cadmium material below about one-eighth inch at the bonding stage. After being substantially completely oxidized, the amount of silver-cadmium oxide present in the portions **18''** and **16** will consist of from about 2 to 17 percent by weight of the material in these portions with the balance being substantially silver. Exemplary percentages of cadmium oxide within this range include 2.6 percent, 5 percent, 10 percent, 13.4 percent, 15 percent and 16.8 percent with the balance in each case being essentially silver.

This material can then be brazed to a suitable backing material such as stainless steel from which an electrical contact can be made.

As an example of the present invention, silver layers may be bonded to each of 0.3 inch thick strips of silver-cadmium alloys having 9 percent and 14.3 percent cadmium by weight respectively of the strips in the following manner:

The strips may be first oxidized in an air atmosphere at a temperature of from 800°–825°C for a period of from 15–20 minutes to achieve a barrier zone **16** of at least 0.001 inches in thickness. To each of these partially oxidized strips a silver layer 0.033 inches may be applied to one of the surfaces thereof by first preparing a sandwich of the strip and the layer, and then hot roll bonding the layer at a temperature of from 775° to 825°C. The strips with the silver layer may be reduced **0.066** inches to achieve a 20 percent reduction in thickness. The rolled strip with the silver layer may then be reduced to a final thickness of 0.125 inches by rolling at ambient temperatures.

The oxidation of the silver-cadmium strips with the silver layer may then be completed by oxidizing the strip in an air atmosphere for a period of from 70–75 hours. The final composition of the contact material will be silver-cadmium oxide strips having about 10 and 15 percent cadmium oxide by weight, each having a silver layer of a thickness of about 0.0125 inches bonded to each strip.

Similar procedures may be used to form silver-cadmium oxide strips with a silver layer bonded thereto for the other percentages of silver-cadmium oxide.

Thus there is described an electrical contact material which can be attached, with better strength of attachment, to a backing material such as stainless steel to form the contact.

What is claimed is:

1. In a method of making an electrical contact material of the Ag-CdO type including the steps of forming a body containing an alloy of Ag-Cd, oxidizing a surface of the body to form a zone including Ag-CdO at the surface of the body, the zone being of a relatively thin thickness in relation to the total thickness of the body, joining a wettable and thermally and electrically conductive material to the Ag-CdO containing zone of the body to form a mass, and internally oxidizing the body to the extent necessary to form a Ag-CdO type material suitable for use as an electrical contact material.

2. In the method of claim **1**, wherein the step of oxidizing the body to form a relatively thin zone containing Ag-CdO at the surface of the body includes the step of subjecting the surface of the body to a heated oxygen containing atmosphere for an effective period of time up to about 30 minutes.

3. In the method of claim **1**, including the additional step of joining a metal containing backing material having good mechanical strength and thermal and electrical conductivity to the wettable and thermally and electrically conductive material.

4. In the method of claim **1**, wherein the wettable and thermally and electrically conductive material is non-oxidizable material.

5. In the method of claim **3**, wherein the wetable and thermally and electrically conductive material is selected from the group consisting of Ag, Au and mixtures thereof, and the backing material is stainless steel.

6. In the method of claim **5**, wherein the wettable and thermally and electrically conductive material is Ag.

7. In a method of making a Ag-CdO electrical contact material including the steps of forming a Ag-Cd alloy body, oxidizing a surface of the body to form a zone of Ag-CdO at the surface of the body, the zone of Ag-CdO being a relatively thin thickness in relation to the total thickness of the Ag-Cd alloy body, joining Ag material to the zone of Ag-CdO at the surface of the body to form a mass, internally oxidizing Cd of the Ag-Cd alloy of the body to the extent necessary to form a Ag-CdO material suitable for use as an electrical contact material, and joining stainless steel to the Ag material joined to the body.

8. In the method of claim **7**, wherein the Ag-Cd alloy body is in the form of strip.

9. In the method of claim **7**, wherein the step of oxidizing the Ag-Cd alloy body to form a zone of Ag-CdO at the surface of the body includes step of subjecting the surface of the body to an oxygen containing atmosphere heated to a temperature of about 700°C to about 850°C for an effective period of time up to about 30 minutes.

10. In the method of claim **7**, wherein the zone of the material suitable for use as an electrical contact material has a coarser CdO particle size than the CdO particle size of the material immediately adjacent to the zone.

11. In the method of claim **10**, wherein the zone of the material suitable for use as an electrical contact material is substantially free of massive amounts of CdO relative to other sections of the body.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,880,608

DATED : April 29, 1975

INVENTOR(S) : F.O. Haarbye

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 4 line 26 Insert "containing" after --cadmium---

Col. 6 line 24 insert "a" after ---is---

Signed and Sealed this

twenty-ninth Day of *July 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks