April 12, 1960 H. R. PFLUMM 2,932,595

SILVER BASE ALLOY FOR USE AS ELECTRICAL CONTACT MEMBER AND METHOD OF MAKING SAME

Filed March 31, 1958

Fig. 1.

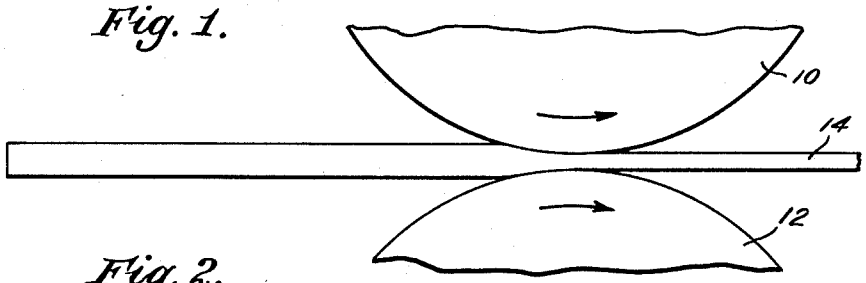


Fig. 2.

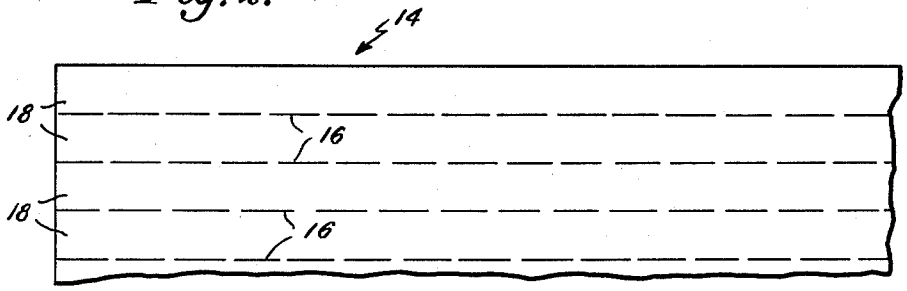


Fig. 3.

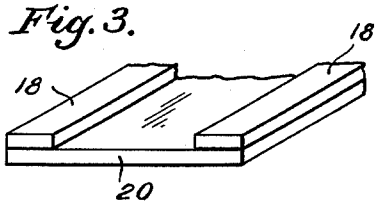


Fig. 4.

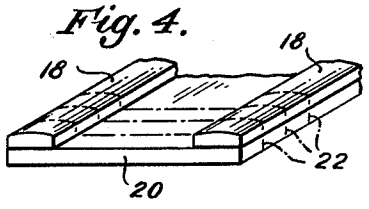


Fig. 5.

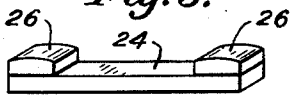
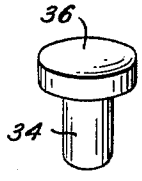


Fig. 6.



Fig. 7.



Inventor,
Heinz R. Pflumm,
by William W. Dalton Jr.
Att'y.

United States Patent Office 2,932,595 Patented Apr. 12, 1960

2,932,595

SILVER BASE ALLOY FOR USE AS ELECTRICAL CONTACT MEMBER AND METHOD OF MAKING SAME

Heinz R. Pflumm, Plainville, Mass., assignor to Texas Instruments Incorporated, a corporation of Delaware

Application March 31, 1958, Serial No. 725,194

9 Claims. (Cl. 148—11.5)

This invention relates to an improved silver-cadmium oxide alloy, to electrical contact elements formed of this improved alloy, and to a method of making the same.

Silver-cadmium oxide contact elements have long been in use by reason of the by now well-known highly beneficial electrical characteristics exhibited thereby. In many, if not most cases, alloys of silver-cadmium oxide are best provided by first forming a silver-cadmium alloy and then internally oxidizing the cadmium. Also, for reasons of economy of production, among others, it is advantageous to fabricate contact elements or other parts of silver-cadmium oxide by conventional melting and mixing procedures followed by mechanical working steps and internal oxidation of the cadmium. The difficulty presents itself, however, that the comparatively high temperatures and long lengths of time of heating to which the silver-cadmium composition must be subjected to internally oxidize the cadmium often results in intergranular cracking of the material. Ordinarily, this integranular cracking results during the oxidation step. In those cases where intergranular cracking during internal oxidation is successfully avoided, such cracking of the material practically invariably occurs during mechanical working thereafter. When the material is internally oxidized after all of the mechanical working steps have been carried out further difficulties ensue as will be pointed out more particularly below.

Accordingly, it would be of substantial advantage to provide an improved alloy capable of being formed by conventional melting and mixing steps, this alloy having substantially the same electrical properties as silver-cadmium oxide and being susceptible of fabrication into parts such as electrical contact members by mechanical working steps; all this while avoiding intergranular cracking of the material whether internal oxidation of the cadmium thereof is carried out before, intermediately of and/or after fabricating the parts. It is an object of this invention to provide such an improved alloy and to provide an improved method of making parts formed thereof.

A further object is to provide such an improved silver-cadmium oxide alloy and method of making parts thereof which are economical, dependable and suited to high capacity commercial production.

A further object of this invention is to provide an improved silver-cadmium oxide alloy capable of being mechanically worked without intergranular cracking thereof.

A further object of this invention is to provide an improved silver-cadmium oxide alloy which is formed by internally oxidizing the cadmium of a silver-cadmium alloy and which is free of intergranular cracking.

Other objects will be in part obvious and in part pointed out hereinafter.

The invention accordingly comprises the ingredients, combinations of ingredients, the proportions thereof and features of composition, the steps and sequence of steps, and features of operation, all of which will be exemplified in the products and methods hereinafter described, and

the scope of the application of which will be indicated in the following claims.

In the accompanying drawings:

Fig. 1 is a more or less diagrammatic side view illustrating the final step of reduction by rolling of a strip of material formed of the improved alloy of this invention according to one exemplary embodiment;

Fig. 2 is a fragmentary view of the rolled strip and showing in broken lines the manner in which this strip is longitudinally slit;

Figs. 3 and 4 are fragmentary perspective views illustrating several subsequent steps in the fabrication of a bridging contactor, Fig. 3 showing two of the longitudinally slit lengths soldered to an elongated base strip and Fig. 4 showing the assembly of Fig. 3 after form rolling of the surface of both of the longitudinally slit lengths and showing in broken lines the manner in which separate parts are successively cut off;

Fig. 5 is a perspective view showing one of the finished bridging contactors after cutting off from the blank of Fig. 4;

Fig. 6 is a plan view of a rod formed by rolling and cold drawing an ingot formed of the improved alloy of this invention, this view showing two blanks as cut off one end of the rod and showing the other end of the rod broken away; and

Fig. 7 is a perspective view of an electrical contact rivet as formed by a heading machine from the rod of Fig. 6.

The new and improved alloy of this invention consists essentially of from 2.5% to 15% by weight of cadmium oxide, a grain refining material composed of cobalt in an amount from an effective trace to 1.5% by weight, and the remainder silver. The smallest percentage by weight of grain refining cobalt that results in the beneficial characteristics ascribed herein to the alloy of this invention is 0.5, and this is what is intended by the term "effective trace." The highest percentage by weight of cobalt attainable by conventional melting and mixing techniques determines the upper limit of the range for this constituent. In this regard, when an excess of 1.5% by weight of cobalt is melted and mixed with cadmium and silver, this excess cobalt rises to the surface of the melt. The cadmium oxide in this improved alloy takes the form of a multiplicity of discrete particles dispersed throughout a matrix of silver; and the grain refining cobalt, being practically insoluble in silver, precipitates out at and lies along the grain boundaries of the silver. Tests have shown that the particular proportion of the amount of the grain refining cobalt to the amount of the remaining constituents of the alloy is immaterial so long as it is within the above-stated range for the reason that no change in properties of the alloy results upon varying this proportion. It is to be understood that the alloy of this invention may include minor percentages of impurities and/or agents which do not deleteriously affect the improved characteristics of the alloy. By way of example, tin in the amount of approximately 0.5% by weight and/or other oxidizable materials could be incorporated into the alloy.

The inclusion of cobalt in silver-cadmium oxide, all in the percentage ranges stated above, has the effect of greatly reducing the grain size of the silver matrix over that which would otherwise result upon internal oxidation of the cadmium of the alloy. This, in large part it is believed, is responsible for the beneficial result that intergranular cracking during oxidation of the cadmium in situ and during mechanical working of the alloy thereafter is avoided. The addition of cobalt also substantially increases the tensile strength and percentage elongation without breaking of the resulting alloy throughout the greater part of the above-stated range of cadmium oxide.

One result of these factors is that the improved alloy of this invention is satisfactorily malleable and capable of being mechanically worked to a very substantial degree throughout almost the entire range of the respective constituents. This is important for the reason that, by virtue of the alloy of this invention, powder metallurgy methods and the inherent difficulties encountered therewith can be avoided. Also, it was necessary previously that internal oxidation of the alloy be effected after fabrication of the material was completed due to intergranular cracking during internal oxidation and thereafter. Because it was previously necessary completely to fabricate the material before internally oxidizing, difficulty was encountered in that oxidation of the alloy causes the material to swell. This swelling results in roughening of the exterior surfaces of the material and leads to difficulty in final sizing of the material to accommodate swelling after oxidation. This is avoided with the improved alloy of this invention in that oxidation of the improved alloy can be carried out intermediately of, and before mechanically working the alloy as well as after so working the alloy without ensuing intergranular cracking thereof. The differences in hardness and yield strength of the alloy of this invention immediately after the internal oxidation step, as compared with, for example, silver-cadmium oxide without any additions, are practically negligible.

In the table below, several of the characteristics of the alloy of this invention are exemplified, the typical value of each of these characteristics for varying percentages of cadmium oxide being indicated. In this regard, each particular embodiment of the alloy is identified by the percentage of cadmium oxide by weight contained therein. The remainder of each alloy embodiment consists of silver with the grain refining cobalt and without cobalt. The first figure (indicated by the legend —Co) for each of the alloy embodiments in this table shows the typical value for each of the respective characteristics after the designated internal oxidation treatment when no cobalt was incorporated in the alloy and the second figure (indicated by the legend +Co) shows the typical value of the respective characteristics after the designated internal oxidation treatment when 0.5% by weight of cobalt was incorporated therein.

Cadmium Oxide, Percent	Internal Oxidation In Air		Grain Size, mm.	Tensile Strength, p.s.i.	Percent Elongation Before Breaking	Yield Strength (.2% offset)	Hardness, Rockwell, 15T Scale
	Time in Hrs.	Temp., ° F.					
2.5—Co	1½	1,500	.120	27,100	25	7,800	48
+Co			.045	33,000	28.5	11,000	57
5—Co	1¾	1,500	.150	28,100	25.5	8,400	52
+Co			.035	33,300	30	10,000	58
7.5—Co	2¼	1,500	.200	27,000	18	7,700	57
+Co			.025	33,000	21.5	12,000	60
10—Co	3½	1,500	.120	30,000	13	15,500	58
+Co			.045	35,300	21	16,200	62
15—Co	7	1,500	.200	30,000	7	12,000	60
+Co			.035	30,800	6	17,000	67

The workability of a composition such as silver-cadmium oxide is largely a function of the percentage elongation before breaking. As noted in the table above, the typical value, in general, of this characteristic of the alloy of this invention decreases (and the hardness increases) with increasing percentages of cadmium oxide. However, the percentage elongation (and tensile strength) are significantly improved by the addition of cobalt up to approximately 12.5% by weight of cadmium oxide, and the grain size is greatly reduced throughout the entire range of the cadmium oxide.

It has been found that the grain refining cobalt addition according to this invention has practically no deleterious effect on either the electrical characteristics of contact members formed therefrom or on the other operational characteristics of such contact members. One of the tests which corroborates this involved testing six pairs of electrical contact elements, each of which pairs was cycled through 25,000 openings and closings thereby correspondingly to open and close a 110 volt, alternating current, 40 ampere circuit. Each of the contact elements contained 10% by weight of cadmium oxide, three pairs of contact elements incorporated 0.5 by weight of cobalt according to the invention and the other three did not, the remainder of each of said contact elements being silver. The average number of welds per pair of contact elements was 22 for the contact elements which included cobalt, and 40 for the contact elements which did not include cobalt. The average electrical resistance after the 25,000 cycles of the contact elements which incorporated cobalt was 0.007 ohm and the average resistance for the contact elements which did not incorporate cobalt was 0.004 ohm.

In producing the improved alloy of this invention, silver, cadmium and the grain refining cobalt are melted and mixed together by conventional techniques and one or more ingots are poured. According to one specific method of making electrical contact elements according to this invention, the ingot is approximately 7" wide, 1¾" thick and 32" long. This cadmium-cobalt-silver alloy is then reduced by rolling down to approximately 0.05" thick. This rolling is illustrated more or less diagrammatically in Figure 1 wherein strip **14** is shown being reduced by rolls **10** and **12**. Strip **14** is then internally oxidized to oxidize the cadmium to cadmium oxide. Roughly, the length of time required for internal oxidation is a function of the thickness of the stock, and for this reason oxidation of the stock according to this example is ordinarily not begun until after the stock has been reduced to the 0.05" thickness. If desired, oxidation of the material could be delayed until a later stage in the fabrication process, or, alternatively, the material could be partially oxidized at this point and finish-oxidized at such a later stage. Internal oxidation is preferably carried out at 1500° F. in ordinary air for a sufficient length of time to oxidize the cadmium. The strip **14** is then slit longitudinally along lines **16** as indicated in Fig. 2 to provide a plurality of longitudinal strips **18** which are approximately 5/16" wide. Two such strips **18** are then solder-bonded to a base strip **20** of brass or copper as shown in Fig. 3. Base strip **20** is approximately 2" in width and approximately equal in thickness to the thickness of each of strips **18**. The assembly is then passed through a set of form-rolls which crown the face of each of strips **18** as indicated in Fig. 4. Subsequently, the assembly is cut successively along lines **22** as shown in Fig. 4 to form a plurality of bridging contactors **24**, each of the contact members of each of the bridging contactors having a crowned face as shown in Fig. 5. It is to be noted that no intergranular cracking is encountered during slitting, form-rolling, cutting off and internally oxidizing, and so long as the cadmium

of contact elements **26, 26** is internally oxidized before the form-rolling step to crown strips **18, 18**, no problems in sizing or roughening arise due to swelling of the material during oxidation thereof.

According to another particular example, silver, cadmium and the grain refining cobalt within the percentage ranges stated above are melted, mixed and cast into cylindrical ingots 1.5" in diameter and 30" long. Each of the cylindrical ingots is cold rolled and then cold drawn down to a rod or wire **30** having a diameter of .090". Preferably at this point, the cadmium is internally oxidized. This is conveniently done by first coiling rod **30** and then placing one or more of such coils in the furnace within which internal oxidation takes place. Rod **30** is then successively cut off into pieces **32** of the desired length and each of the pieces is swaged in a conventional header machine to form a contact rivet **34** having a head **36** as shown in Fig. 7. Because oxidation of the stock is carried out before the blanks are headed, the face of the contact is smoth, no particular problem in sizing of the contact due to swelling is incurred, and further, no sticking together of individual contact members occurs as would otherwise occur if the internal oxidation step were to be carried out on a batch of mutually contiguous members.

Where final sizing and/or roughening of the exterior surfaces present no problem because either or both of these characteristics are not important in the finished product, internal oxidation can dependably be carried out after (as well as during and before) mechanical working without inter-granular cracking of the alloy of this invention.

Due to the conversion of cadmium to cadmium oxide during the internal oxidation process, the density of the resulting alloy of this invention is less after oxidation than before the cadmium-cobalt-silver alloy is oxidized. To accommodate this, a percentage by weight of cadmium smaller than the resulting percentage by weight of cadmium oxide must be alloyed with cobalt and silver. The change in percentage by weight of cobalt during oxidation of the cadmium due to the change in density is negligible. The table below shows the values of the percentage by weight of cadmium necessary to provide the given percentage by weight of cadmium oxide after oxidation, and for each of the latter this table shows the density of the alloy in grams per cubic centimeter before and after oxidation.

Cadmium, Percent by Weight	Resulting Percent of Cadmium Oxide by Weight	Density Before Oxidation, g./cc.	Density After Oxidation, g./cc.
2.19	2.5	10.43	10.41
4.41	5.0	10.39	10.33
6.60	7.5	10.33	10.26
8.87	10.0	10.29	10.19
13.39	15.0	10.18	10.04

It is to be clearly understood that the improved results of this invention are realized only during and after internal oxidation of the cadmium of the initially-formed silver-cadmium-cobalt composition. A cadmium-silver alloy even when the proportions of the cadmium and silver constituents lie within or close to the cadmium oxide and silver constituents of a given cadmium oxide-silver alloy (the latter being such as would result by internally oxidizing the cadmium of the former) is very greatly different from a corresponding silver-cadmium oxide alloy, and the role played by the cobalt incorporated in the silver-cadmium oxide alloy according to this invention is to this same extent altogether different from that when incorporated in cadmium-silver before internal oxidation of the cadmium of the latter. By way of example, a silver-cadmium oxide alloy incorporating 2.5% to 15% by weight of cadmium oxide (without cobalt) possesses a relatively low degree of malleability as compared with the corresponding initially-formed silver-cadmium alloy (before internal oxidation of the latter to provide the former).

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As many changes could be made in the above compositions, articles and methods without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. An electrical contact member consisting essentially of 0.5% to 1.5% by weight of a grain refiner composed of cobalt, 2.5% to 15% by weight of cadmium oxide and the remainder silver, the cadmium oxide being in the form of particles dispersed throughout the silver and the grain refining cobalt being disposed along the grain boundaries of the silver.

2. An electrical contact member formed of an alloy consisting essentially of 0.5% to 1.5% by weight of a grain refiner composed of cobalt, 2.5% to 15% by weight of cadmium oxide and the remainder silver; having a structure obtained by internal oxidation of the cadmium; said alloy being characterized by a tensile strength, percent of elongation before breaking and yield strength which are substantially higher than that of an internally oxidized silver cadmium oxide alloy formed without the addition of a grain refiner.

3. An alloy characterized by its mechanical workability without intergranular cracking and by its fine grain size, said alloy consisting essentially of from an effective trace to 1.5% by weight of cobalt, 2.5% to 15% by weight of cadmium oxide and the remainder silver, the cadmium oxide being in the form of particles dispersed through the silver, and the cobalt being disposed along the grain boundaries of the silver.

4. The method comprising the steps of alloying by melting and mixing 0.5% to 1.5% by weight of a grain refiner composed of cobalt, substantially 2.15% to 13.39% by weight of cadmium and the remainder silver, fabricating the product of said first step by a plurality of mechanical working steps and internally oxidizing the cadium.

5. The method as set forth in claim 4 wherein the step of internally oxidizing the cadmium is carried out prior to the final step of said plurality of mechanical working steps.

6. The method of making electrical contact members, said contact members being formed of an alloy consisting essentially of 0.5% to 1.5% by weight of a grain refiner composed of cobalt, 2.5% to 15% by weight of cadmium oxide and the remainder silver; said method comprising melting and mixing the grain refining cobalt, cadmium and silver in the proportions subsequently to provide the desired percentage by weight of each of cobalt, cadmium oxide and silver within the respective said percentage ranges; and then internally oxidizing the cadmium of the product of said melting and mixing step and mechanically working said product to fabricate and finally size the contact members.

7. The method as set forth in claim 6 wherein the step of internally oxidizing the cadmium is carried out prior to final sizing of said contact members.

8. The method as set forth in claim 4 wherein the step of internally oxidizing the cadmium is carried out subsequent to the final step of said plurality of mechanical working steps.

9. In the method of alloying a composition which is to be internally oxidized, which composition consists of

2.15% to 13.39% by weight of cadmium and the remainder silver, the step of adding 0.5% to 1.5% by weight of cobalt.

References Cited in the file of this patent

UNITED STATES PATENTS

2,313,070 Hensel et al. ---------- Mar. 9, 1943

2,539,298 Doty et al. ---------- Jan. 23, 1951

2,796,346 Stumback ---------- June 18, 1957

FOREIGN PATENTS

807,416 Germany ---------- June 28, 1951