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[54] **SILVER-METAL OXIDE COMPOSITE AND METHOD OF MANUFACTURING THE SAME**

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[58] **Field of Search**...................... 75/173 R, 173 C

[56] **References Cited**

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[57] **ABSTRACT**

The composite comprises a silver matrix having grain boundaries and metal oxide grains enriched at said grain boundaries of said silver matrix. An alloy is provided, which comprises silver, a second metallic component, and at least two alloying metals selected from the class consisting of calcium, antimony, magnesium, beryllium, aluminum, tin, manganese, and zirconium. Said second metallic component and said alloying metals are oxidized in said alloy to form said composite.

10 Claims, No Drawings

SILVER-METAL OXIDE COMPOSITE AND METHOD OF MANUFACTURING THE SAME

The invention relates to a silver-metal oxide composite, in particular silver-cadmium oxide, for use on contact pieces in low voltage switching apparatus, and to a method for its manufacture.

Silver-metal oxide composites, preferably silver-cadmium oxide with 6 to 15% by weight CdO, have been used for quite some time as contact-surfacing material in low voltage switch apparatus. The advantage of these materials in relation to pure silver is a considerably lesser likelihood of welding during the switching operation, an arc-quenching effect — which is essentially based on prevention of the resistance sparking of alternating current switch arcs — and normally a longer service life in the switching arc.

In the manufacture of such materials, one known method is to mix mechanically powders of silver and cadmium oxide and to seal the powder mixture in a single pressing technique to the contact pieces which are then sintered below the melting point of silver. This method of manufacture is hereinafter referred to as P1.

The contact materials produced in this way have a favorable welding behavior but inadequate resistance to ignition loss (see Metall 6, 1952, page 369). Even the addition of other oxides increased the service life only by a small amount (U.S. Pat. No. 2,796,346, British Patent Specification No. 683,343). The method of single pressing always produces highly porous brittle compound bodies with coarse oxide coatings and is therefore used in cases in which it is of more importance to ensure a high resistance to welding than a high resistance to ignition loss of the contacts, for example, in aviation switch units with low switch voltages.

Significantly better silver-cadmium oxide materials can be made by internal oxidation of melted homogenous silver-cadmium alloys (this method hereinafter being referred to as O1). For the majority of low voltage switch units such as air-break contactors, motor-protective switches and cable protection switches, this oxidation method represents a marked advance, at least as regards the ignition loss of the contacts (see U.S. Pat. No. 2,673,167; Metall 10, 1956, page 628).

The quality of the contact materials AgCdO with A CdO content of 6 to 15% by weight which are produced by internal oxidation, is mainly determined by the form in which the CdO is precipitated. It is generally considered that the best material was that in which the CdO was finely granulated and uniformly distributed throughout the volume. Thus one hoped to avoid in the case of interruption of the oxidation the formation of linear CdO precipitates and/or with CdO concentrations in the grain boundaries and heterogenous confining of CdO agglomerates the tendency towards zones of low material strength and increased friction.

With a view to refinement of the grains it was therefore proposed, for example, that grain-refining additives such as Ni, Co, Fe, Mo, Cr, Ti, Sn, Zn and V should be added in very small quantities (0.001 to 1 weight %) to the AgCd alloy (see German Patent Specification No. 1,153,178; British Patent Specifications Nos. 1,032,398 and 2,796,346)) and/or that there should be an increase in the partial oxygen pressure during oxidation in order to ensure uniform precipitation and to make the brittle material deformable.

Only in the applications mentioned above, in which the resistance to ignition loss is of less importance than the welding characteristics, were additives to cause embrittlement ever used, for example, Mg (U.S. Pat. No. 2,669,512).

The micrograph of a material which was produced in accordance with the method O1 shows homogenous distribution of the CdO particles (grain size D = 5 microns). Such a structure was generally considered a prerequisite for optimal resistance to ignition loss since CdO concentration in the grain boundaries of the silver considerably weakens the matrix and leads in the switching operation to a destruction of the contact pieces along the grain boundaries.

These requirements are met by a more recent method of manufacture (hereinafter referred to as P2) in a powder metallurgical process in which a mixture filling of very finely distributed silver and cadmium oxide is sintered to blocks and then sealed by heat deformation using for example rollers or extrusion presses (see Metallkunde 58, 1967, page 752; German Patent Publication P1,539,848,8).

It was therefore generally assumed that silver-metal oxide composites attain their highest degree of resistance to melting loss when the oxide particles were distributed as homogenously as possible in the silver matrix.

In contrast to this generally held opinion in the technology it has been shown, rather surprisingly, in the course of an extensive investigation of the contact behavior of internally oxidized silver-metal oxide composites that in some cases silver-cadmium oxide composites with very high grain boundary concentrations and striking brittleness of the contact pieces can result in an extraordinarily long service life even under severe conditions. The behavior of this material contradicts all previous experience and cannot at the moment be scientifically explained.

Therefore, according to the present invention, in a method of manufacturing a material having a silver matrix from a silver-metal base alloy, in particular a silver-metal oxide composite for use in contact pieces, the silver matrix is formed having in its structure concentrated metallic oxide grains at its grain boundaries, and the alloy comprises at least two of the following alloying metals: Ca, Sb, Mg, Be, Al, Sn, Mn, Bu and Zr.

The oxide precipitation of the new contact material of the invention produces extremely finely granulated ($D < 0.1$ micron) material, preferably in the grain boundaries of the silver matrix and in a considerably less extent in the Ag grain.

This type of precipitation is obtained by an addition of at least two of the metals Ca, Li, Sb, Mg, Be, Al, Sn, Mn, Bi and Zr to the Ag/Cd base alloy.

Ignition loss characteristics well above the average are shown by the following internally oxidized alloys (oxidation in oxygenated atmosphere at 600° to 850° C.):

Ag–Cd 10 – Ca 0.7 – Sn 0.6 – Ni 0.2
Ag–Cd 11 – Sn 1 – Ca 0.3 – Ni 0.3
Ag–Cd 12 – Sb 0.5 – Sn 0.5 – Ca 0.3
Ag–Cd 12 – Sn 0.5 – Ca 0.3
Ag–Cd 12 – Sb 0.5 – Sn 0.5
Ag–Cd – Be 0.3 – Ca 0.3

The materials produced are brittle and can be deformed only with great difficulty.

The brittleness alone is, however, not an adequate criterion for a high resistance to ignition loss. An addition of for example 0.1 weight % Mn alone to the AgCd alloy increases the hardness and the brittleness of the oxidized material considerably, but at the same time reduces the service life to about half that of a AgCdO material without additives which is easily deformable. Only the addition of a second element of the series listed above produces the unexpected effect.

EXAMPLE

From 86.7% Ag, 12% Cd, 0.5% Sb, 0.5% Sn and 0.3% Ca (all % by weight) an alloy is molten in an electrically heated furnace and cast in bar form. The soft bars are smoothed down and after repeated rolling and intermediate annealing at 650° C. in inert gas with a silver plate in accordance with known roller plating methods, so that they can subsequently be perfectly soldered to the contact supports. From the still soft plate the contact discs are now punched, for example, in dimensions of 16 × 16 × 2.1 mm. These contact discs are now internally oxidized for 11 days at 700° C. under a pressure of 1 atmosphere above atmospheric pressure. The contact discs become brittle as a result. The structure of the silver matrix is fine-grained. On the grain boundaries the extremely small metallic oxide particles have collected together.

The service life of contact discs made from material produced in this manner is apparent from table 1 and it is there shown in comparison with AgCdO qualities which were produced in accordance with the powder metallurgical method P1 and P2or by internal oxidation of a known alloy O1.

TABLE 1

In this table are shown on the right-hand side the highest possible numbers of switching operations as a measure of the service life of AgCdO contact pieces of the same shape which were produced in accordance with the manufacturing method shown on the left. The contact pieces were installed in an air-break contactor and the switching operations were carried out to switch an A.C. current of U = 380 volts, I = 310 amp., on and off, cosy = 0.38, in touch contact operation with 600 switch operations per hour.

Material produced as per process:	Maximum number of switching operations:
AgCdO 12 as per P1	60,000–120,000
AgCdO 12 as per O1	210,000–280,000
AgCdO 12 as per P2	300,000–450,000
Material according to the invention	500,000–750,000

Apart from the considerably longer service life, the appearance of the contact parts after this extreme load is noteworthy. The surface of the contact pieces made from the new material is in spite of the appearance of many microscopic cracks very uniformly eroded and in comparison with the surface of contact pieces made from AgCdO which have been produced by the known methods, it shows no silver concentration nor droplets of welded material at the edge.

For these reasons, namely (1) low ignition loss (2) uniform ignition loss and (3) no formation of droplets of welded material, the material of the invention is suitable, in contrast to the known AgCdO materials as per P1, P2and O1, for fast-switching low voltage switches.

What is claimed is:

1. Method of manufacturing a brittle, homogeneous silver-cadmium oxide composite having grain boundaries and metal oxide grains enriched at said grain boundaries in a silver matrix, which comprises: (1) mixing together to form an alloy silver, cadmium and at least two other alloy components selected from the group consisting of calcium, antimony, magnesium, beryllium, aluminum, tin, manganese, and zirconium, and (2) internally oxidizing said alloy in an oxidizing atmosphere at a temperature from about 600°C to about 850°C to precipitate extremely finely granulated oxide material in the grain boundaries of the silver matrix, the proportions by weight of components in said composite being from about 6% to about 15% of cadmium oxide, and from about 0.5% to about 6% of each oxide of said other alloy components.

2. Method according to claim 1, wherein the oxides of each of said other alloy components are present in amounts of from about 0.5% to about 2% by weight.

3. Method according to claim 1, wherein said alloy is formed from 86.7% silver, 12% cadmium, 0.5% antimony, 0.5% tin, and 0.3% calcium, all of said percents being by weight.

4. Method according to claim 1, wherein said alloy is formed from 88.5% silver, 10% cadmium, 0.7% calcium, 0.6% tin, and 0.2% nickel, all of said percents being by weight.

5. Method according to claim 1, wherein said alloy is formed from 87.4% silver, 11% cadmium, 1% tin, 0.3% calcium, 0.3% nickel, all of said percents being by weight.

6. Method according to claim 1, wherein said alloy is formed from 86.7% silver, 12% cadmium, 0.5% antimony, 0.5% tin, 0.3% calcium, all of said percents being by weight.

7. Method according to claim 1, wherein said alloy is formed from 87.2% silver, 12% cadmium, 0.5% tin, 0.3% calcium, all of said percents being by weight.

8. Method according to claim 1, wherein said alloy is formed from 87% silver, 12% cadmium, 0.5% antimony and 0.5% tin, all of said percents being by weight.

9. Method of manufacturing contact pieces for low voltage switching which comprises (1) forming an alloy from silver, cadmium and at least two alloy metals selected from the group consisting of calcium, antimony, magnesium, beryllium, aluminum, tin, manganese, and zirconium, (2) shaping said alloy into electrical contact pieces of desired size and shape, (3) internally oxidizing the contact pieces of said aloy in an oxidizing atmosphere at a temperature from about 600°C to about 850°C to precipitate extremely fine granulated oxide material in the grain boundaries of the silver, the proportions by weight of components in said oxidized alloy being from about 6% to about 15% of cadmium oxide, and from about 0.5% to about 6% of each oxide of said alloy metals, and (4) recovering the oxidized contact pieces suitable for long life low voltage switching operations.

10. Composite of silver-cadmium oxide with at least two oxides of alloy metals selected from the group consisting of calcium, antimony, magnesium, beryllium, aluminum, tin, manganese, and zirconium, said composite consisting essentially of a silver matrix, fine grains of oxide less than 0.1 micron diameter in the grain boundaries of the silver matrix and in considerably less extent in the silver grain, the amounts by weight of components other than silver in said composite being from about 6% to about 15% cadmium oxide, and from about 0.5% to about 6% of each of said oxides of alloy metals.

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