

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

Publication number:

**0 441 018 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21)

Application number: **90301383.7**

(51)

Int. Cl.<sup>5</sup>: **C22C 32/00, C22C 1/10,  
H01H 1/02**

(22)

Date of filing: **09.02.90**

(43)

Date of publication of application:  
**14.08.91 Bulletin 91/33**

(84)

Designated Contracting States:  
**DE ES FR GB IT SE**

(71)

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**Ag-SnO electrical contact materials and manufacturing method thereof.**

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Ag-SnO electrical contact materials are disclosed, which are made of Ag alloys consisting of 5-20 weight % of Sn and a balance of Ag, the alloys having been prepared by melting and having been internal oxidized. Novel manufacturing methods are also disclosed, in which internal-oxidation is conducted in an oxygen atmosphere of 10 atm to 200 atm, and at a temperature of 750 °C to 500 °C.

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**AG-SNO ELECTRICAL CONTACT MATERIALS AND MANUFACTURING METHOD THEREOF****Background of the Invention**

This invention relates to electrical contact materials which are used for electrical contacts employed in electrical apparatuses such as switches, breakers, contactors, and the like.

5 Electrical contact materials dealt with in this invention are particularly those made of Ag-Sn alloys which are made by melting Ag and Sn and which are internally oxidized. Those belong to a different category from those which are prepared by mixing Ag and SnO powders and powdermetallurgically sintering them.

Heretobefore, Ag-Sn oxides alloys in which Ag is a matrix and Sn, solute metal thereof is internal-oxidized to Sn oxides, are widely used as electrical contact materials for the electrical apparatuses of the  
10 kind mentioned above.

As a similar electrical contact material, Ag-Cd oxides alloys are known, while electrical contact materials made of Ag-Sn oxides alloys are more extensively employed today in view of the prevention of pollution, since Cd is harmful to health.

However, there is a serious problem in the manufacture of Ag-SnO alloy contact materials. That is, it is  
15 impossible to completely internal-oxidize a total amount of Sn by oxygen which penetrates from the outside of Ag matrix and diffuses into the inside of the matrix, if said Sn is more than about 5 weight % of the Ag matrix. This is a phenomenon commonly accepted by those skilled in this art. And, for example, it is described in the Information (registration No. 1-11) published by DODUCO of west Germany in April, 1966 that in Ag-Sn alloys containing more than 5% of Sn, this Sn can not be oxidized by an internal oxidation  
20 method. It is pointed out there that this is because of segregation layers of Sn oxides which are inevitably formed at outer surface areas of such alloys and retard oxygen to penetrate into the alloys for developing the internal oxidation in inner areas. As mentioned above, this has been conceived unanimously by those skilled in industries related to electrical contact materials.

In order to solve this problem, it becomes necessary for a successful internal-oxidation to employ  
25 auxiliary solute metals which have higher diffusion velocities or which are more capable to carry oxygen and to convey the oxygen more efficiently into deeper inner areas of Ag matrices. Such auxiliary solute metals are typically In and Bi.

There is issued U.S. Patent No. 3,933,485 in which Ag-Sn-In system alloys are internal-oxidized for obtaining modern electrical contact materials, and in which In is used as an auxiliary solute metal for the  
30 successful internal-oxidation of the alloys. Said electrical contact materials which are more specifically consisted of 5-10 weight % of Sn, 1.0-6 weight % of In, and a balance of Ag, and are internal-oxidized. They are one of the most excellent contact materials which are industrially used today.

Nevertheless, even when In which can perform well internal-oxidation assisting functions, as explained above, is employed as an auxiliary solute metal, it is not easy to internal-oxidize more than 5% of Sn evenly  
35 throughout its Ag matrix. It is sometimes observed that Sn oxides happen to segregate excessively at outer surface areas of the Ag matrix, and such segregation makes subscales which are air-tight, while a depletion layer of Sn oxides is consequently produced in inner areas of the Ag matrix.

It has been noted also that since InO and BiO have a comparatively lower refractoriness, and are comparatively weak metal oxides, it has been desired long since to internal-oxidize Ag-Sn alloys without the  
40 employment of In or Bi, if possible.

It will be noted also that compared to secondary Ag-Sn alloys, Ag-Sn-In alloys and Ag-Sn-Bi alloys which are tertiary, are provided with lower electrical conductivities. In this respect too, it is preferable not to use In or Bi as auxiliary elements for the sake of internal-oxidation.

**Brief Summary of the Invention**

In view of the above, this invention is to provide entirely novel electrical contact materials which are prepared by melting, are consisted of 5-20 weight % of Sn and balance of Ag, only, and are internal-oxidized.

50 As to a Sn amount in this invention, its minimum is 5 weight % in order to afford the obtained electrical contact materials with efficient refractoriness, and its maximum is 20 weight %, because if Sn is given in an amount more than 20 weight %, the resultant materials will be too brittle. In this invention, though it is characteristic that secondary Ag alloys which are added only by Sn and prepared by melting, are internal-oxidized, one or more elements selected from iron family elements (Fe, Co, and Ni) may be added to said secondary Ag alloys. Such addition is not for the acceleration or assistance of internal-oxidation, but merely

for fining or minuting alloy crystalline structures of the resultant alloys. In order to achieve this end, iron family elements will be added at an amount of 0.001-1 weight %.

This invention is also to provide a novel method for preparing the above-mentioned novel electrical contact materials.

5 To wit, it has been discovered by the present inventors through a large number of experiments that those Ag-Sn (5-20 weight %) alloys which had been impossible to be internal-oxidized, can successfully and completely be internal-oxidized when an oxygen atmosphere for the internal-oxidation is made more than 10 atm. This is novel knowledge and judgement first acquired by the present inventors.

10 It has been known that in the manufacture of electrical contact materials by internally oxidizing Ag alloys, their Ag matrices are heated so that they become active to induce outside oxygen thereinto. A heating temperature for this end is commonly in a range of 500-750 °C. In this connection, it has been also found by the present inventors that while Ag-Sn (5-20 weight %) alloys can be internal-oxidized in an oxygen atmosphere of more than 10 atm as discovered by them, the above-mentioned heating temperature shall preferably be made comparatively lower within the above-mentioned range of temperature, when the  
15 oxygen atmosphere is selected higher. This is because that if the oxygen atmosphere and the heating temperature are both high, Ag matrices become excessively active and consequently take thereinto oxygen too much, resulting in making an oxidation velocity of Sn in the Ag matrices too fast and in producing subscales at surface areas of the Ag matrices on account of the segregation of Sn oxides thereabout. In other words, when the oxygen atmosphere pressure is made comparatively low above 10 atm, the heating  
20 temperature will preferably be made high within the above-mentioned range of about 500-750 °C. And, on the contrary, it is preferable that when the oxygen atmosphere is comparatively high above 10 atm, the heating temperature will be made low within the above-mentioned range of internal-oxidation heating temperature.

When Ag alloys of the above-mentioned specific constituents are internal-oxidized in accordance with  
25 this invention, it is also preferable to conduct the internal-oxidation at such condition where the Ag alloys are kept at a solid phase not involving any liquid phase, since if the alloys become liquid even partially, metal oxides precipitated by then might move about floatingly towards surface areas of the alloys and subsequently make subscales thereabout.

In view of the above, when the heating temperature is sided low within the above-mentioned range of  
30 temperature or near to its minimum temperature of about 500 °C, it is better to make the oxygen atmosphere as much as higher. But, in order to prevent the alloys from becoming liquid and on account of safe and economic industrial and commercial operations, the maximum oxygen atmosphere preferably employable in this invention will be up to about 200 atm. In other words, when Ag-Sn (5-20 weight %) alloys made by melting are internal-oxidized in accordance with this invention, the lower and upper or minimum  
35 and maximum oxygen atmosphere shall preferably be 10 atm and 200 atm, and its heating temperature shall preferably be in a range of about 750 °C to about 500 °C.

### **Preferred Embodiments**

40 This invention is explained in a further concrete manner in the following examples.

(1) Ag-Sn 6 weight %

(2) Ag-Sn 6 weight %-Ni 0.2 weight %

The above constituents (1) and (2) were melted and made to ingots of 120mm in diameter and 40mm in length. The ingots were hot-extruded into square bars of 30mm in thickness and 50mm in width. The bars  
45 were then cut to a length of 500mm each, and their upper and lower surfaces were shaved by a thickness of 3mm each to obtain square bars of 24mm in thickness, 510mm in width, and 500mm in length.

To each lower surface of the square bars, there were bounded pure silver of 2.5mm in thickness. They were rolled by pressure so that they had thickness of 1.2mm. By punching them by a punch having a cutting hole of 6mm in diameter, disk-shaped contact materials backed by the pure silver and having 6mm  
50 diameter and 1.2mm thickness were obtained.

They were internal-oxidized by heating them 700 °C for 48 hours in an oxygen atmosphere of 25 atm.

Vertical sections of the resulted contact materials were observed through a microscope to the effect that there was produced no subscales at and about surface areas of the materials, and that Sn constituents were completely oxidized. It was observed also that particles of Sn oxides were extremely fine and were  
55 precipitated evenly in their Ag matrices, irrespectively of Ag grain boundaries of the Ag matrices. Precipitation distribution and structures of Sn oxides were thus extremely fine, as if they were prepared by powder-metallurgical methods.

In order to make a comparison, the following alloy (3) was made. Contact materials which are made by

the internal oxidation of said alloy (3) are known as one of the today's best electrical contacts having extremely excellent contact characteristics and performance.

(3) Ag-Sn 6 weight %-In 1 weight %-Ni 0.2 weight %

This alloy which had been prepared by melting, was processed into disk-shaped contact materials same to those specified in the above (1) and (2) alloys.

The disk-shaped contacts were internal-oxidized by heating then to 620° C for 24 hours at a normal oxygen atmosphere of 1 atm.

The resultant contacts (3) were observed by a microscope, similarly to the contacts (1) and (2). It was found that Sn was completely internal-oxidized in this contacts too, while they were precipitated squamously along Ag grain boundaries, and were noticeably coarse than those of the contacts (1) and (2).

Hardness (HRP) and electrical conductivity (IACS%) of the above internal-oxidized contact materials (1), (2), and (3) were as follows.

	Hardness	Electrical conductivity
( 1 )	78	72
( 2 )	80	70
( 3 )	95	55

Welding times by anti-welding tests (conducted under electric voltage of DC 240V, initial electric current (discharge current from a condensor electric current) of 700A, contact pressure of 200g, and test cycles of 20) were as follows.

( 1 )	0
( 2 )	0
( 3 )	0

Amounts of consumption (mg) by ASTM test method (by electric voltage of AC 200V, electric, current of 50A, contact pressure of 400g, and releasing force of 600g) were as follows.

( 1 )	10
( 2 )	8
( 3 )	15

As described and explained above in detail, this invention can provide absolutely novel electrical contact materials made of Ag-Sn (5-20 weight %) alloys which has been prepared by melting and internal-oxidized. As readily known from the above test data, the electrical contact materials made in accordance with this invention are substantially secondary Ag-Sn alloy provided with Sn oxides precipitated extremely finely and evenly in its Ag matrix and, consequently having excellent contact properties including their improved electrical conductivities.

### Claims

1. Ag-SnO electrical contact materials made of Ag-Sn (5-20 weight %) alloys which have been prepared by melting and which have been internal-oxidized.
2. Ag-SnO electrical contact materials as claimed in claim 1, alloys of which are added by one or more elements selected from iron family elements (Fe, Co, and Ni) at an amount of 0.001-1 weight %.

3. Ag-SnO electrical contact materials as claimed in claims 1 or 2, alloys of which have been internal-oxidized in an oxygen atmospher of more than 10 atm and at a condition where the alloys were kept at a solid phase not involving any liquid phase.
- 5 4. Ag-SnO electrical contact materials as claimed in claims 1, 2, or 3, alloys of which have been internal-oxidized by heating them in an oxygen atmosphere of 10 atm-200 atm to a temperature of 750-500 ° C.
5. Manufacturing method of Ag-SnO electrical contact materials, which comprises internal-oxidizing Ag-Sn (5-20 weight %) alloys which have been prepared by melting, by heating them in an oxygen  
10 atmosphere of more than 10 atm and at a condition where said alloys are kept solid so that they do not contain any liquid phase.
6. Manufacturing method of Ag-SnO electrical contact materials as claimed in claim 5, in which the alloys are added by one or more elements selected from iron family elements (Fe, Co, and Ni) at an amount  
15 of 0.001-1 weight %.
7. Manufacturing method of Ag-SnO electrical contact materials as claimed in claims 5 or 6, in which the oxygen atmosphere is 10 atm to 200 atm.
- 20 8. Manufacturing method of Ag-SnO electrical contact materials as claimed in claims 5, 6, or 7, in which a temperature of heating is 750 to 500 ° C.

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# EUROPEAN SEARCH REPORT

Application Number

EP 90 30 1383

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 111 (C-577), 16th March 1989; & JP-A-63 286 558 (TANAKA KININZOKU) 24-11-1988 ---	1	C 22 C 32/00 C 22 C 1/10 H 01 H 1/02
Y	IDEM ---	2-4	
Y	FR-A-2 522 191 (CHUGAI DENKI KOGYO) * Claims 1-2; page 3, lines 18-39; page 4, example * ---	2	
Y	US-A-4 150 982 (A. SHIBATA) * Column 2, line 54 - column 3, line 29 *	3-4	
A	US-A-4 243 413 (A. SHIBATA) * Column 3, example 1 * -----	3-4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 22 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-10-1990	Examiner SCHRUERS H.J.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</p>			