

# **54. IWK**

Internationales Wissenschaftliches Kolloquium International Scientific Colloquium

Information Technology and Electrical Engineering - Devices and Systems, Materials and Technologies for the Future



Faculty of Electrical Engineering and Information Technology

Startseite / Index: http://www.db-thueringen.de/servlets/DocumentServlet?id=14089



## Impressum

Herausgeber: Der Rektor der Technischen Universität Ilmenau Univ.-Prof. Dr. rer. nat. habil. Dr. h. c. Prof. h. c. Peter Scharff

Redaktion: Referat Marketing Andrea Schneider

> Fakultät für Elektrotechnik und Informationstechnik Univ.-Prof. Dr.-Ing. Frank Berger

Redaktionsschluss: 17. August 2009

Technische Realisierung (USB-Flash-Ausgabe): Institut für Medientechnik an der TU Ilmenau Dipl.-Ing. Christian Weigel Dipl.-Ing. Helge Drumm

Technische Realisierung (Online-Ausgabe): Universitätsbibliothek Ilmenau <u>ilmedia</u> Postfach 10 05 65 98684 Ilmenau

Verlag:

## isle

Verlag ISLE, Betriebsstätte des ISLE e.V. Werner-von-Siemens-Str. 16 98693 Ilmenau

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ISBN (USB-Flash-Ausgabe): ISBN (Druckausgabe der Kurzfassungen): 978-3-938843-45-1 978-3-938843-44-4

Startseite / Index: <a href="http://www.db-thueringen.de/servlets/DocumentServlet?id=14089">http://www.db-thueringen.de/servlets/DocumentServlet?id=14089</a>

## IMPROVED SILVER/TIN OXIDE FOR AUTOMOTIVE APPLICATIONS

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#### ABSTRACT

The requirements pertaining to the electrical load and service life of relays and switches used for automotive applications are becoming more and more stringent.

In order to meet these requirements, the existing silver / tin oxide (Ag/SnO<sub>2</sub>) material with indium oxide (In<sub>2</sub>O<sub>3</sub>), produced by the melting metallurgy method and subsequent internal oxidation, was developed further. By optimizing manufacturing equipment and the stages of the process, an improved Ag/SnO<sub>2</sub> (with In<sub>2</sub>O<sub>3</sub>) with a very fine microstructure was developed.

Electrical test results show very low and regular material transfer and low erosion during service life tests, even with inductive loads. In addition, no sticking or welding occurred with capacitive loads.

## **1. INTRODUCTION**

The requirements pertaining to the electrical load and service life of relays and switches used for automotive applications are becoming more and more stringent. The reasons for this are to be found in the greater use of electrical functions for safety, economy and comfort features in cars [1]. For example, flasher relays were previously required to switch a maximum of two flasher lights simultaneously. Nowadays, the car's flasher relay has to switch four or more lights simultaneously every time the doors are locked or unlocked. The relay for the windshield wiper did not previously have to switch very often in manual mode but more often in intermittent mode. Because of the use of modern technology such as rain sensors, the relay now has to switch much more frequently throughout its entire service life.

In order to meet these more demanding requirements, the existing silver / tin oxide  $(Ag/SnO_2)$  material with indium oxide  $(In_2O_3)$  produced by the melting metallurgy method and subsequent internal oxidation, was developed further.

 $Ag/SnO_2$  with  $In_2O_3$  is a common contact material in the Asian market [3], [4], [5]. Currently, the demand

for these materials for inductive DC and some special AC applications is also increasing in Europe. It is known that the amount of  $In_2O_3$  has an influence on switching behaviour [6]. The addition of  $In_2O_3$  to Ag/SnO<sub>2</sub>, produced by the melting metallurgy method performs two functions – firstly, it is necessary for the internal oxidation manufacturing process and secondly, it has a positive effect on switching behaviour.

By optimizing the manufacturing equipment and the stages of the process it was possible to produce an improved  $Ag/SnO_2$  with  $In_2O_3$  with a very fine microstructure and consequently with improved switching behaviour.

This paper focuses on the switching behaviour of  $Ag/SnO_2$  contact materials with different additives and made by different manufacturing processes in a model switch and in a relay applying various electrical loads.

#### 2. EXPERIMENTAL

## 2.1 Contact materials

The contact materials investigated in this paper are listed in table 1.

The internally oxidized (i.o.) contact materials Ag/SnO<sub>2</sub> 12 and Ag/SnO<sub>2</sub> 14 were produced by melting different Ag-Sn-In alloys in a protective atmosphere and subsequent casting and oxidation. The alloy compositions were designed to yield a total oxide content of 12 wt% and 14 wt%, respectively. By improving the oxidation process, it was possible to obtain a very fine microstructure. The microstructures of the standard contact material Ag/SnO<sub>2</sub> 12 TOS is shown in figure 1 and Ag/SnO<sub>2</sub> 12 TOS F is shown in figure 2. The comparison shows a very fine and uniform distribution of the oxides in the case of the internally oxidized TOS 12 F material.

All other contact materials (p.m.) with a total oxide content of 12 wt% were produced by blending powders, pressing a billet, extrusion and subsequent drawing. Ag/SnO<sub>2</sub> 12P has no further additive besides the respective oxide component. The Ag/SnO<sub>2</sub> 12PE has bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) and

No.	Material	Silver content / wt%	Additives	Electrical conductivity / m/Ωmm <sup>2</sup>	Vickers hardness / HV5	Remarks
1	Ag/SnO <sub>2</sub> 12P	88	-	45 - 47	63	p.m.
2	Ag/SnO <sub>2</sub> 12PW	88	WO <sub>3</sub>	45 - 46	64	p.m.
3	Ag/SnO <sub>2</sub> 12PE	88	Bi <sub>2</sub> O <sub>3</sub> , CuO	45 - 46	65	p.m.
4	Ag/SnO <sub>2</sub> 12TOS	88	In <sub>2</sub> O <sub>3</sub>	44 - 46	96	i.o.
5	Ag/SnO <sub>2</sub> 12TOSF	88	In <sub>2</sub> O <sub>3</sub>	44 - 46	95	i.o.
6	Ag/SnO <sub>2</sub> 14TOSF	86	$In_2O_3$	42 - 44	98	i.o.

Table 1: Contact materials (p.m. = powder metallurgy, i.o. = internal oxidation)

copper oxide (CuO) and  $Ag/SnO_2$  12PW has tungsten oxide (WO<sub>3</sub>) as additives besides the respective oxide component. For a comparison of the typical micro section of the p.m. contact materials see figure 3.

In order to study the mechanical behavior of the contact materials, tensile samples were deformed using an Instron testing machine operating at a constant cross head velocity of 3 mm / min (nominal axial strain rate 5 x  $10^{-4}$  sec<sup>-1</sup>). The physical properties of the contact materials are given in table 1.



Figure 1: Micro section of Ag/SnO<sub>2</sub> 12 TOS



Figure 2: Micro section of Ag/SnO<sub>2</sub> 12 TOS F

For all samples the typical parabolic stress strain curves are seen to be normal for particle reinforced materials as shown in figure 4. However, the tensile strengths of the internally oxidized materials are at least 40 to 80 MPa greater when compared to the p.m. materials. Furthermore, all i.o. materials have a higher ductility than the p.m. materials.

The contact materials were made into composite rivets with a head diameter of 2.8 mm.



Figure 3: Micro section of Ag/SnO<sub>2</sub> 12 P



Figure 4: Stress/strain curves of p.m. and i.o. materials

## **3. ELECTRICAL TESTS**

#### 3.1 Model switch tests

3.1.1 Setup of the model switch

The equipment (i.e. model switch control and evaluation software and hardware) is designed to meet the requirements of the typical automotive 14 V DC power net [1].

The movable contact (anode) is driven by a linear actuator. Depending on the length of the contact gap, an opening velocity of max 0.5 m/s was obtained. The parameters used are as follows:

- Contact force: approximately 1 N;
- Contact gap: 0.5 mm;
- Opening velocity: 0.1 m/s.

The movement of the linear drive was controlled by a personal computer. By means of a spring/damper system with a fixed contact (cathode), a reproducible contact bounce at make ( $t_{bounce} = 450 - 500 \ \mu s$ ) was achieved.

## 3.1.2 Electrical tests with model switch

For the electrical tests a power supply with a maximum rating of 70 A at 60 V DC was used. The electrical tests were carried out with artificial load circuits (e.g. adjustable resistors and air-core coils) given in table 2.

In order to characterize the switching behavior of the contact materials, the following electrical tests were performed. Electrical service life tests were run with two different inductive loads. The electrical service life test sequence (i.e. linear motor control and data acquisition and evaluation) was controlled by a personal computer and run automatically.

Load	Ia	I b	
Load voltage U / V	14	14	
Load current I <sub>on</sub> / A	25	25	
Load current I <sub>off</sub> / A	25	25	
Inductance L / mH	0.5	1	
t <sub>on</sub> / t <sub>off</sub> / sec	0.3 / 1.7	0.3 / 1.7	
Ambient temperature	room temperature		

Table 2: Electrical loads used (model switch)

While make parameters and therefore make bouncing were kept constant for all tests, the make bouncing and the break arc were monitored by means of a transient measurement PCI card. With every load cycle, the voltage U(t) and current I(t)curves by current probe, contact travel a(t) and contact force F(t) were measured by the transient measurement card. The program includes the evaluation and storage of the number of contact bounces, the bouncing time, bouncing energy, arc duration, arc energy, opening and closing velocity, contact resistance, contact force and contact welding force.

After 50,000 make and break operations the test was stopped and the mass changes at the anode and cathode were determined gravimetrically.

## 3.2 Automotive relay tests

3.2.1 Relay description

The service life tests were performed with the commercial plug-in type relay "Power F4" [7] for automotive applications. The joining of the contact rivets as well as the assembly of the relays was carried out under normal factory mass-production conditions. Rivets used for the stationary and movable contact were composites as described in 2.1.

The typical relay parameters (all values refer to the contact level) are as follows:

- Contact arrangement: make contact (1 Form A);
- Contact force: approximately 200 cN;
- Contact gap: 0.5 mm;
- Release force (normally open contact opens): 50 cN;
- Polarity: movable contact: anode / fixed contact: cathode.

## 3.2.2 Electrical tests with the relay

To evaluate the new contact materials, both inductive and capacitive loads were tested.

Capacitive load types for automotive applications, such as front and rear beams, flasher and filter capacitors in electronic modules mainly stress the contact material during switch-on. Capacitive loads (current profile show in figure 5) have a high current inrush combined with a remarkable arc during bouncing and a low steady current. The electrical life tests were run with a current inrush of 200 A and a current break of 20 A.

Inductive load types for automotive applications, such as heater blower, cooling fan and window lifter particularly stress the contact material. Inductive loads (current profile shown in figure 6) are characterized by a relatively slow current increase at make and a remarkable switch-off arc at break, induced by the demagnetization of the magnetic circuit of the load. The electrical life tests were run with three typical load types, shown in table 3.

All tests were performed with an electric life endurance tester; each switching operation was monitored for reliable closing and opening of the contacts. The load characteristic was simulated by electronic load simulation. The first failure was monitored.



Figure 5: Current profile of capacitive DC load tested



Figure 6: Current profile of inductive DC loads tested

Load	II a	II b	II c
Load voltage U / V	13.5	13.5	13.5
Load current I <sub>on</sub> / A	80	90	140
Load current I <sub>off</sub> / A	33	30	50
Inductance L / mH	0.25	0.125	0.1
t <sub>on</sub> / t <sub>off</sub> / sec	1/3	1 / 1	1/3
Ambient temperature / °C	-40 to +85 (2 h)		

Table 3: Inductive loads used (relay)

## 4. TEST RESULTS

#### 4.1 Model switch

The test results under load I b with tests as described above are summarized in figures 7 and 8. The test results under load I a are similar to the results of load I b, the differences are not so distinctive.

Contact erosion, either loss or transfer of contact material for 1,000 make and break operations is shown in figure 7. The 5 %, 50 % and 95 % quantile values of contact resistance recorded during electrical service life tests are charted in figure 8.



Figure 7: Contact erosion and material transfer with test Ib for 1,000 operations (25 A, 1 mH, 50,000 operations)



Figure 8: Contact resistance during service life at test Ib (25 A, 1 mH, 0 to 50,000 operations)

## 4.2 Automotive relay

4.2.1 Capacitive load

All tests were terminated at the required service life without failures and revealed no differences between the contact materials. Therefore the data base does not allow a definitive statement concerning the differences between the tested contact materials. Additional tests will be carried out.

#### 4.2.2 Inductive load

The results of the first failure are summarized under load IIa (80A / 33A / 0.25mH) in figure 9, under load IIb (90A / 30A / 0.125mH) in figure 10 and under load IIc (140A / 50A / 0.1mH) in figure 11. All three figures show the Weibull distribution of failure probability through the first failure during the service life test. For a direct comparison between the materials tested the switching cycles in the diagram were scaled to the first missing operation of all relays (relative factor = no. of operations of the first failure / min. no. of operations in this test).



Figure 9: Weibull distribution of failure probability through the first failure under load IIa,(80 A / 33 A / 0.25 mH)



Figure 10: Weibull distribution of failure probability through the first failure under load IIb (90 A / 30 A / 0.125 mH)



Figure 11: Weibull distribution of failure probability through the first failure under load IIc (140 A / 50 A / 0.1 mH)

#### **5. DISCUSSION**

#### 5.1 Contact erosion / Material transfer

Figures 12 and 13 show micro sections of  $Ag/SnO_2$  12 TOS and TOSF after service life, load II b. The contact erosion is due to the high arc energy at break. A material transfer is observed from the anode to the cathode.

Under inductive load IIb,  $Ag/SnO_2$  12TOSF shows less contact erosion than  $Ag/SnO_2$  12TOS even after twice service life (see figure 10). In addition  $Ag/SnO_2$  12TOSF shows erosion of very low tendency to crater/pip-formation. So obviously the fine oxide particle distribution has a positive effect on the erosion of  $Ag/SnO_2$  12TOSF.



*Figure 12: Micro section of Ag/SnO*<sub>2</sub> *12TOS* (movable contact: anode) under load IIb (90 A / 30 A / 0.125 mH), first failure after 5.6 (relative factor)



Figure 13: Micro section of Ag/SnO<sub>2</sub> 12TOSF (movable contact: anode) under load IIb (90 A / 30 A / 0.125 mH) first failure after 10.5 (relative factor)

Under load IIc  $Ag/SnO_2$  12PW shows a higher tendency to material transfer than  $Ag/SnO_2$  12TOSF (see figures 14 and 15).

Also with load II c Ag/SnO<sub>2</sub> 12TOSF (see figure 14) shows low material transfer and no crater/pip-formation.

Comparing  $Ag/SnO_2$  12P and 12PW (see figure 15) the additive  $WO_3$  improves the switching behavior in respect of anti-welding behavior but does not improve properties such as contact erosion or material transfer with special inductive loads as shown in figure 7.



Figure 14: Micro section of Ag/SnO<sub>2</sub> 12TOSF (fixed contact: cathode) under load IIc (140 A / 50 A / 0.1 mH), first failure after 5.9 (relative factor)



Figure 15: Micro section of Ag/SnO<sub>2</sub> 12PW (fixed contact: cathode) under load IIc (140 A / 50 A / 0.1 mH), first failure after 2.5 (relative factor)

## 5.2 Anti-welding properties / first failure

Typical first failures are generated by a sticking of the contacts. The contacts no longer open within a

specific time. This is influenced by separation of silver and tin oxide forming tin oxide layers as shown in figures 16 and 17 at the contact surface due to the action of the arc.

 $Ag/SnO_2$  12PW (see figure 16) shows a no great tendency towards the separation of silver and tin oxide or to the formation of tin oxide layers. The lower area (1) shows the original microstructure obtained by extrusion. The upper area (2) close to the contact surface shows fine tin oxide particles dispersed in Ag even after the melting and resolidification of the Ag.

After a very long service life under load II b, Ag/SnO<sub>2</sub> 12TOSF (see figure 17) starts to show the formation of silver-rich layers ① and tin oxide lines ② in the contact material on its surface. The tin oxide lines can elevate high contact resistance and the silver layers can cause the first failure. The lower area ③ shows the original microstructure.



Figure 16: Micro section of Ag/SnO<sub>2</sub> 12PW (movable contact: anode) under load IIa (80 A / 33 A / 0.25 mH), first failure after 5.6 (relative factor)



Figure 17: Micro section of Ag/SnO<sub>2</sub> 12TOS F (movable contact: anode) under load IIb (90 A / 30 A / 0.125 mH) first failure after 10.5 (relative factor)

#### 6. SUMMARY

The results are summarized in table 4.

According to table 4  $Ag/SnO_2$  12 P without any additive demonstrates a tendency to material transfer and erosion. Additives such as  $Bi_2O_3$  and CuO in  $Ag/SnO_2$  12 PE and WO<sub>3</sub> in  $Ag/SnO_2$  12 PW noticeably improve the anti-welding behavior. These two materials are recommended for normal inductive loads where Ag/SnO2 12 P is not sufficient.

Contact materials	Material erosion / transfer		Contact resistance		First failure (relay)		
Load (table 2 & 3)	Ia	Ib	Ia	Ib	IIa	IIb	IIc
Ag/SnO <sub>2</sub> 12P	+	+	+	+	0	*	0
Ag/SnO <sub>2</sub> 12PW	+	0	+	+	+	*	+
Ag/SnO <sub>2</sub> 12PE	+	+	+	+	*	*	*
Ag/SnO <sub>2</sub> 12TOS	++	++	+	+	*	0	*
Ag/SnO <sub>2</sub> 12TOSF	++	++	+	+	++	++	+
Ag/SnO <sub>2</sub> 14TOSF	++	++	+	+	*	*	*

Table 4: Summary, Loads: see table 2 & 3 ++ = very good; + = good; 0 = average \* not tested

Ag/SnO<sub>2</sub> 12 TOS F and Ag/SnO<sub>2</sub> 14 TOS F show the best overall performance for high inductive DC loads, where a low and regular contact erosion and low material transfer over a high service life is required (14 TOS F: preliminary failure results in a model switch). In addition, no sticking or welding with capacitive loads occurs. Furthermore they have a higher ductility than materials produced by powder metallurgy methods.

#### 6.1 Outlook

After proving that a reduction in oxide particle size leads to improved switching behavior, the effect of the total oxide content is to be evaluated. Internally oxidized Ag/SnO<sub>2</sub> materials with oxide contents ranging from 8 wt% to 14 wt% will therefore be subject of future work.

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