Comparison of properties of silver-tin oxide electrical contact materials through different processing routes

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In the present work silver-tin oxide ($\text{Ag-SnO}_2$) electrical contact materials have been prepared by different processing techniques, viz., powder metallurgy (P/M), internal oxidation (I/O) and internal oxidation of alloyed powders (IOAP). The influence of processing routes on the physical properties such as electrical conductivity, density and microstructure of these $\text{Ag-SnO}_2$ composite materials are compared. The microstructural study reveals that internal oxidation (I/O) technique provides most uniform structure.

Key words: Electrical contact materials, internal oxidation, silver tin oxide

Electrical contact materials are used in many electromechanical devices as component which can carry current intermittently through contact surfaces. The basic properties required for these materials are that they should possess high electrical and thermal conductivity, high melting point and good oxidation resistance. High melting point is required to avoid any accidental overheating because of fusion of the contact points whereas high thermal conductivity helps to dissipate heat effectively. In order to keep the contacts clean and free of insulating oxides, it is essential that material must possess good oxidation resistance. Metals like gold, silver, copper, palladium and their alloys; composites of silver and copper with various metal oxide combination are being used in various low and high voltage switchgears\textsuperscript{1,2}.

Silver metal oxide composite electrical contact materials find application in low voltage switchgear devices such as contactors, relays, circuit breaker and switches\textsuperscript{3,5}. Several composite systems like $\text{Ag-CdO}$, $\text{Ag-ZnO}$, $\text{Ag-NiO}$, $\text{Ag-CuO}$, $\text{Ag-SnO}_2$ and $\text{Ag-SnO}_2$-$\text{InO}_2$ are the materials which are currently in use\textsuperscript{6-8}. Efforts are being made to develop new alloy system to achieve improved performance. Silver cadmium oxide has been on the center stage for several decades after having made its debut in 1950\textsuperscript{9-11}. It has been well established that $\text{Ag-CdO}$ composites are suitable for switching devices operating in the range of 15-5000 A\textsuperscript{12, 13}. However, because of toxic nature of cadmium and of increasingly stricter environmental regulation imposed by RoHS (restriction of hazardous substances, the European Union Directive 2002/95/EC) and WEEE (waste electronic and electrical equipment in electrical and electronic equipment set at July 2006 by European Union), considerable efforts are underway to develop Cd free silver metal oxide materials. In this regard, the oxides of tin, zinc and indium are under investigation\textsuperscript{14-21}. Among this $\text{Ag-SnO}_2$ has emerged as a substitute of $\text{Ag-CdO}$ as it has superior corrosion resistance and better anti welding properties as compared to $\text{Ag-CdO}$. $\text{Ag-SnO}_2$ derives its improved anti-corrosion characteristics from thermally stable tin oxide which prevents melting and scattering on the surface of the contact by electric arc generated during contact movement\textsuperscript{21-25}. Since $\text{Ag-SnO}_2$ is a combination of two dissimilar materials, namely, a metal and an oxide, process routes other than the conventional melting are followed to manufacture these materials. Earlier reported work\textsuperscript{26} on erosion behaviour on silver-metal oxide have shown that a continuous increase in temperature from 45°C to 85°C occurs for
a switching operation between 2-16 kilo cycles for Ag-SnO\textsubscript{2} alloys whereas very little fluctuation was observed for Ag-CdO and Ag-ZnO alloys when tested under similar conditions. The reason for it was non-uniform dispersion of SnO\textsubscript{2} phase in silver matrix. Apart from this the eroded surface exhibited volcanic craters, which is because of segregation of SnO\textsubscript{2} phase along grain boundaries thus exposing the silver matrix, which is soft, and get eroded\textsuperscript{26}. Currently two methods are being commercially used to provide a dispersion of tin oxide particles in silver. One method which is used by German companies is the internal oxidation of silver-tin alloys\textsuperscript{19,27}. At the same time Japanese companies follow the powder metallurgy process where mixing of tin oxide with silver powder followed by pressing and sintering is done to achieve fine dispersion of tin oxide in the matrix of silver\textsuperscript{26}. The above methods have some limitations like formation of needle like brittle phase and limitation of oxidation\textsuperscript{27,28}. Considering the above fact the present study is undertaken to develop Ag-SnO\textsubscript{2} contact material with uniform distribution of second phase SnO\textsubscript{2} in the silver matrix.

**Experimental Procedure**

Ag-SnO\textsubscript{2} composite contact materials are prepared by powder metallurgy (P/M), internal oxidation (I/O) and internal oxidation of alloyed powders (IOAP techniques) by taking 5N purity elements and 4N purity compounds. The composition of composite made by above techniques is given in Table 1.

The P/M involves thorough mixing of fine powders of silver and tin oxide in a ball mill. The mixed powder is consolidated and pre-sintered to increase density. However, in order to achieve high final density, secondary processes, such as repressing, sintering and extrusion are essential. The details of these processes followed in the present investigation are given in the flow chart as shown in Fig. 1. The (I/O) process essentially consists of preparation of silver-tin-indium alloy by induction melting under vacuum. The alloy is rolled in the form of sheets of suitable thickness and homogenized subsequently. Pieces of suitable size and dimensions are punched out from the homogenized sheet and internally oxidized. Indium was added to silver-tin alloy to facilitate internal oxidation. The flow chart of the process adopted is shown in Fig. 2. In the IOAP process, which is a hybrid of I/O and P/M processes described earlier silver-tin-indium alloy was prepared by induction melting. The melt was subsequently atomized in an indigenously designed and fabricated atomizer\textsuperscript{29}. The powders collected after atomization

![Flow chart of powder metallurgy process (P/M)](image)

**Table 1— Important physical properties of Ag-SnO\textsubscript{2} materials processed by different techniques**

<table>
<thead>
<tr>
<th>Process</th>
<th>Composition</th>
<th>Conductivity (% IACS)</th>
<th>Hardness (HV 1.0)</th>
<th>Density g/cm\textsuperscript{3}</th>
<th>%Theoretical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder metallurgy</td>
<td>Ag-10 SnO\textsubscript{2}</td>
<td>64</td>
<td>89.2</td>
<td>9.6</td>
<td>97%</td>
</tr>
<tr>
<td>Internal oxidation</td>
<td>Ag-7.6 SnO\textsubscript{2} –4.8 In2O3</td>
<td>62</td>
<td>111.0</td>
<td>9.9</td>
<td>100%</td>
</tr>
<tr>
<td>Internal oxidation of alloyed powder</td>
<td>Ag-7.6 SnO\textsubscript{2} –4.8 In2O3</td>
<td>59</td>
<td>87.2</td>
<td>9.7</td>
<td>99%</td>
</tr>
</tbody>
</table>
are subsequently internally oxidized. The internally oxidized powders are used for making the contact points of different shapes and dimensions by P/M techniques. The flow chart of the process is shown in Fig. 3. The details of these processes are described elsewhere\textsuperscript{26}.

Test pieces of 16 mm diameter were prepared from the lot of samples prepared in each route. The electrical conductivity of samples was measured with eddy current conductivity meter. To minimize the error in measurement, the samples were carefully polished on 600 grit emery paper before measurement. The hardness was measured with the help of Vickers hardness tester (Buahler, USA). The reported hardness values are an average of five readings. Density was measured by dimensional arrangement. In order to study the microstructure, the samples were mechanically polished and observed under scanning electron microscope (SEM). All the microstructures were taken in back scattered electron mode of the microscope.

**Results and Discussion**

The physical properties of the contact materials prepared by different process routes are compared in Table 1. It can be noticed that P/M route gives higher electrical conductivity despite of fact that 3% porosity in the material exists. The pores are potential scattering centers for the electrons and consequently reduce the conductivity\textsuperscript{26}. However, P/M processed materials without any pore are likely to exhibit higher conductivity due to better connectivity. On the other hand, despite of its better density, the I/O composites show poor conductivity. This can be attributed to the straining of silver lattice resulting from the formation of bulky tin oxide and indium oxide particles. The strain in lattice changes the mean free path of electrons and hence the conductivity. The lowest value of conductivity observed in I/O is the result of pores as well as lattice strain in these materials. It is evident from Table 1 that I/O has the best hardness. High value hardness is attributed to the full density and very uniform distribution of tin oxide and indium.
oxide in silver. P/M suffers from the disadvantage of density and relatively poorer dispersion of oxide and consequently the poor hardness. IOAP has the similar features as that of P/M.

The I/O process suffers from the problem of high inter-diffusion of tin in silver. It has been established that a high content of tin (>4wt%) in silver is not amenable to internal oxidation as it forms an impervious layer of tin oxide, inhibiting further diffusion of oxygen into the alloy. In order to facilitate oxidation, several additives such as bismuth, copper and indium have been tried with different measures of success. Among these, the indium bearing the silver-tin alloy has been commercially exploited to its full potential. Indium prevents the formation of dense oxide bands of SnO$_2$ and enables oxygen to diffuse at faster rate into the silver-tin alloys.

The material resulting from such process leads to a fine dispersion of In$_2$O$_3$ and SnO$_2$ in the matrix of silver. This dispersion of oxides in the matrix of silver provides high hardness and reasonably good electrical conductivity. The greatest disadvantage of the process stems from the slow diffusion of oxygen in the material resulting in higher process time. Use of indium escalates the cost. Moreover, the internally oxidized materials invariably have an oxide free zone also called denuded zone in the center and non-uniform microstructure across the depth. Because of the small size of the powders, the time for internal oxidation is reduced to a great extent. The material processed by this route exhibit good electrical conductivity and hardness. The material also displays uniform microstructure and is devoid of denuded zone.

The microstructure of the materials developed by P/M, I/O and IOAP are given in Figs 4, 5 and 6 respectively. As is evident from the microstructure, I/O gives the most uniform microstructure. However, I/O has the problem of oxides precipitating along the grain boundaries. This can be controlled to some extent by reducing the solute percentage. I/O sometimes also has features of divorced grain boundary, i.e., region close to grain boundary are devoid of oxides. The pores and state of dispersion of oxides in P/M processed material are shown in Fig. 4. Better connectivity of individual silver grains is revealed in the microstructure.

Figure 6 shows the microstructure of the IOAP processed material. It may be noted that a silver-rich region envelopes each grain. The silver-rich region enveloping each grain is the result of diffusional creep of silver following the formation of bulky SnO$_2$ and In$_2$O$_3$ inside the lattice. This silver-rich region facilitates sintering and gives rise to better connectivity.
Conclusions
From the above work it can be concluded that P/M and IOAP processes are less time consuming but require large infrastructure with more processes steps. The materials processed by P/M route exhibit homogenous microstructure, high electrical conductivity and greater latitude in composition selection and overall faster speed of process. However, the materials processed by P/M route show poor hardness and density. At the same time I/O requires less process step with uniform microstructure and full density. Thus, a judicious selection of the process for the production of the tips requires a trade-off between properties, investment and scale of operation.

References
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