

Novel Method for Preparation of Silver-Tin Oxide Electrical Contacts

H. Chang, C.H. Pitt, and G.B. Alexander

A novel method of coating tin oxide particles with silver by an electroless plating process has been developed to produce silver-tin oxide electrical contact materials. A powder metallurgy process has been developed to consolidate the electroless plated silver-tin oxide composite powders. The effect of the various plating conditions on the morphology of the composite powder was studied using the transmission electron microscope (TEM) and the scanning electron microscope (SEM). An optical microscope and electron microprobe analysis (EMPA) were used to characterize the structure of the sintered silver-tin oxide compact. Ductility and hardness were measured to ensure that the mechanical properties are adequate, and electrical conductivity was also measured.

1 Introduction

MOST of the electrical contact materials in use today contain cadmium oxide particles that are volatile and toxic. Because of the fact that vaporization of cadmium oxide during switching could be detrimental to workers' health, its use in contact materials has been banned by health organizations in some other countries. To replace the cadmium oxide, many foreign companies have utilized tin oxide in silver electrical contacts.[1-6]

Recently in the United States, research on the replacement of silver-cadmium oxide by silver-tin oxide has been attempted by many investigators. Comparing the erosion behavior, the silver-tin oxide material had less steady-state erosion, better weld resistance, and higher contact resistance compared to silver-cadmium oxide.[2-7] Silver-tin oxide composites are used in low-voltage switching devices, aircraft relays, motor starters, circuit breakers, etc.[8,9] From these investigations, it may be concluded that materials based on silver-tin oxide are the likeliest candidates to replace silver-cadmium oxide-type materials. This composite can prevent arc erosion created during the making and breaking of circuits carrying large currents. It has also been observed that the zones melted by the arc are smaller and the viscosity of the molten material is higher in the silver-tin oxide-type material, resulting from the higher thermal stability of the tin oxide, which tends to reduce material loss by splashing of melt drops by the arc.[6]

Two methods have been used commercially to provide a dispersion of tin oxide particles in silver. One method used by German companies is the internal oxidation of a silver-tin alloy.[10] Another method followed by Japanese companies involves a powder metallurgy approach that consists of mixing tin oxide with silver powder and pressing and sintering the compact.[11] Each of these methods has drawbacks in the successful production of silver-tin oxide composites. In the internal oxidation process, the tin oxide produced near the surface provides a surface barrier to further oxidation in alloys containing more than about a 10 vol.% tin. In the powder metallurgy process, the tin oxide particles grow in a needlelike morphology during the sintering process and produce a highly brittle product.[12]

One approach to solving the problem of producing silver-tin oxide composites would be to make a tin oxide sol and completely coat the colloidal particles with silver in an aqueous solution by an electroless plating (ELP) process. The powders could then be separated from solution, pressed, and sintered to produce a silver-tin oxide composite. This silver-tin oxide electrical contact should have good electrical conductivity, arc erosion resistance, and proper ductility and hardness. One could also readily control the amount of tin oxide desired in the composite.

One of the objectives of the present study was to determine if a dense coating of silver could be deposited from an aqueous solution on individual particles of a colloidal oxide to produce a silver-tin oxide composite for electrical contacts by means of electroless plating. Another objective was to develop the best powder metallurgy process for producing a silver-tin oxide composite and to correlate the mechanical and electrical properties of this composite with the volume loading of the tin oxide and the morphology of electroless plated composite powders.

By carrying out these experiments, it was possible to review the data to determine what useful electroless plating conditions and consolidation conditions would be suitable for a commercial electrical contact material. The development of a nontoxic silver-tin oxide for use in contacts for the electrical industry was a prime goal of this research.

2 Experimental Methods

2.1 *Preparation of Tin Oxide Colloidal Particles*

To prepare a tin oxide sol by the peptization technique, reagent-grade tin oxide powder was ball milled in an ammonical solution. Twenty grams of tin oxide powder were placed in 200 ml of deionized water containing 3 ml of concentrated ammonia. The mixture was placed in a polyethylene bottle containing 300 g of 4-mm-diameter stainless steel balls and rotated for 12 hr. The colloidal tin oxide particles were examined in a transmission electron microscope (JEM-200CX STEM, JEOL).

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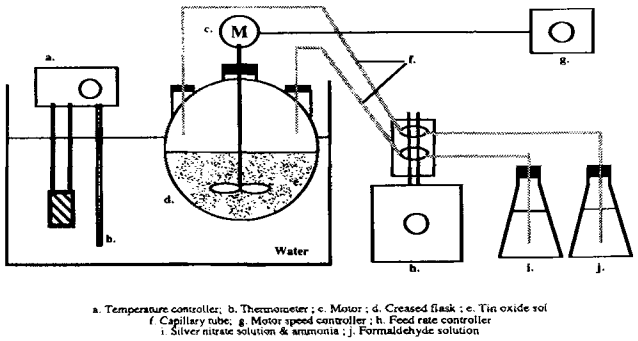

a. Temperature controller; b. Thermometer ; c. Motor ; d. Creased flask ; e. Tin oxide sol
f. Capillary tube; g. Motor speed controller ; h. Feed rate controller
i. Silver nitrate solution & ammonia ; j. Formaldehyde solution

Fig. 1 Experimental setup for laboratory-scale electroless silver plating on tin oxide particles in aqueous solution.

2.2 *Electroless Plating of Silver on Tin Oxide Particles in Aqueous Solution*

Attempts were made to plate silver on tin oxide particles in an aquasol by an electroless plating process. This was done by introducing a soluble salt (silver nitrate) and a reducing agent (formaldehyde) into a dilute solution of the tin oxide aquasols during vigorous stirring. The experimental setup is shown in Fig. 1. To obtain suitable stirring, a creased flask equipped with a stirrer was used. Solutions of silver nitrate and formaldehyde were introduced into the flask through capillary tubes whose feeding was restrained to a constant rate by a digital unified drive. Temperature was controlled with a thermostat, and pH was adjusted using ammonium hydroxide. Volume loading of tin oxide by 15% was initially tried followed by 2, 5, and 10 vol.% loading.

In each batch, 5 g of silver-tin oxide composite powders was produced. Temperature, silver ion concentration, silver ion feed rate, pH, and formaldehyde concentration were variables in the electroless plating process. The factorial-designed experiment identified the optimum conditions for producing a fine and uniform size of silver-tin composite powder without powder agglomeration. The other objective of this experiment was to develop a low-cost process with a high-quality product.

Silver-15 vol.% tin oxide composite powders, for instance, were prepared by the following procedures. The peptized tin oxide particles (0.584 g) were suspended in 350 ml of deionized water, and several drops of ammonia produced a colloid. The tin oxide colloidal sol was placed in a creased flask in a water bath of 50 °C for more than 30 min with continuous stirring. Silver nitrate 0.23 mole solution was prepared by dissolving 7.87 g of silver nitrate in 200 ml of deionized water. Ammonia was added to this solution to control the pH at 9.5. Formaldehyde 0.5 mole solution was also prepared. These two solutions were fed into the tin oxide colloidal sol through the capillary tube with a feed rate of 2.3 mmole of silver ion per minute. The reacted solutions were vigorously stirred during the electroless plating. After the reaction was finished, the silver-plated composite powders were carefully filtered. The powders were then rinsed and dried in the air for 12 hr at 120 °C, followed by heating in argon for 2 hr at 250 °C.

A scanning electron microscope (HITACHI S-500 SEM) was used to investigate the morphology and the appearance of the electroless plated silver-tin oxide composite powders. The change in the powder size and the microstructure were investigated as a function of bath temperature, reagent concentration, and feed rate.

To determine that the tin oxide particles were completely coated with silver, X-ray analyses of the powders were made in the scanning electron microscope by energy dispersive analysis of X-rays with an X-ray energy spectrometer (KEVEX 5500). Warren's method[13] was also used to determine the crystal size of the silver coating. The X-ray diffraction peaks of the composite powder were used to calculate the line broadening from the silver crystallites.

2.3 *Powder Consolidation*

The electroless plated silver-tin oxide composite powders were consolidated by a conventional powder metallurgical process, *i.e.*, compaction-sintering. Secondary working was done on the sintered compact. A heat treated stainless steel die of 8-mm inside diameter was used for preparing 1-g pellets in each compaction with pressures of 500 to 750 MPa. A cylindrical shape was obtained by the double action of the pistons in a hydraulic press.

The compacted pellets were placed on the flat surface of alumina D-tube and sintered at different temperatures for 1 to 3 hr in an air atmosphere. The sintered silver-tin oxide composite pellets were examined with a scanning electron microscope (HITACHI S-500 SEM) and an optical microscope (LECO NEOPHOT 21 Large Incident-Light Camera Microscope). No etching was needed to observe the tin oxide dispersion in the sintered matrix. The oxide dispersions were analyzed by utilizing electron microprobe analysis on the microprobe (CAMECA SX-50), and the back-scattered X-ray from the tin oxide particles was also examined.

Hardness was measured using a microhardness tester (LECO M-40 Hardness Tester) by applying a 100-g load for making a Vickers diamond pyramid hardness indentation. Ductility estimations were made simply by cold rolling the sintered pellet until a crack appeared on the pellet, after which the reduction of thickness before cracking was determined. Density was also measured with a specific gravity flask.

From these experiments, an optimal consolidation technique for making the best electrical contact material was determined. More pellets were compacted and sintered by using silver-tin oxide composite powders that have different amounts of tin oxide loading. Mechanical properties were measured again on these composites, and electrical conductivity was also measured to evaluate the effect of the amount of tin oxide on those properties. For studying the effect of secondary working, the sintered pellets were repressed and annealed at 350 °C for 30 min, followed by measuring hardness and density.

3 Results and Discussion

3.1 *Characterization of Tin Oxide Colloidal Particles*

Colloidal tin oxide particles were prepared by a peptization technique. The powers were ball milled, and these agglomerated particles were converted to stable tin oxide colloidal sols

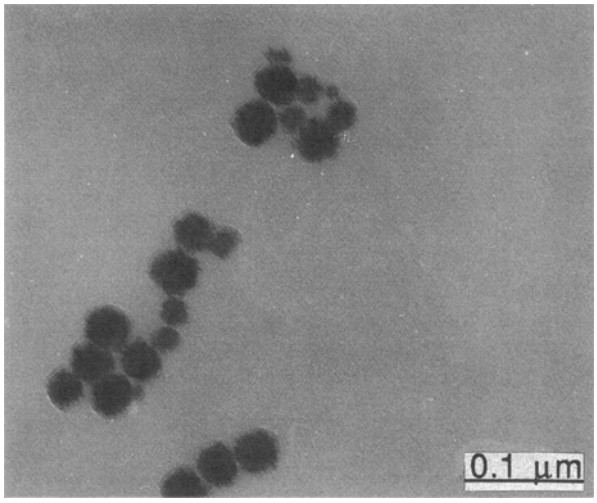

Fig. 2 Transmission electron micrograph of tin oxide colloidal particles.

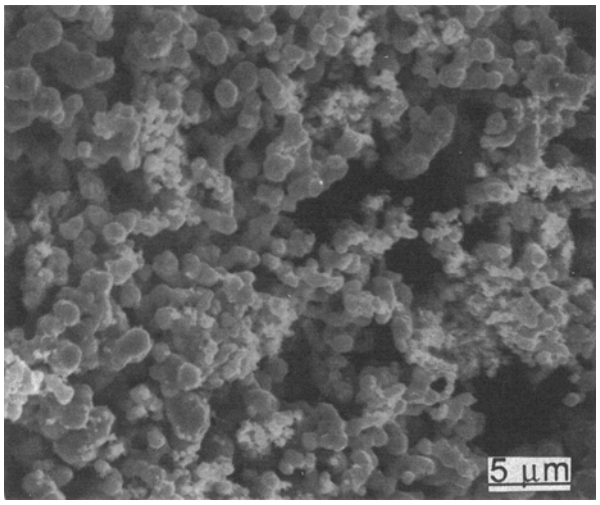

Fig. 3 Scanning electron micrograph of silver-15 vol.% tin oxide composite powders.

by treating them with aqueous ammonia. The particles took on a negative charge on the surface by adsorption of hydroxyl ions so that the particles were not agglomerated. The product obtained is shown in the transmission electron micrograph in Fig. 2. The individual tin oxide particles were 0.05 μm in diameter, and they were nicely dispersed in an aqueous solution.

3.2 *Development of Electroless Plating Process*

An objective of studying the electroless plating process of silver on colloidal tin oxide was to determine if silver could be deposited successfully on the tin oxide particles and whether the microstructures of the resulting composites could be controlled. If a continuous, dense coating of silver could be deposited on individual particles, the ductility of the resulting composites would be high. When silver ions were reduced in the presence of colloidal oxides in aqueous solutions, the silver would deposit on colloidal nuclei.

In the process, a reducing agent (formaldehyde) and a silver solution (silver nitrate) are reacted in the presence of tin oxide. The partial reactions in this electroless silver plating system are:

$$2Ag^{+} + 2e^{-} \rightarrow 2Ag \quad [1]$$

and

$$HCHO + 3OH^{-} \rightarrow HCOO^{-} + 2H_2O + 2e^{-} \quad [2]$$

with the overall reaction being:

$$2Ag^{+} + HCHO + 3OH^{-} \rightarrow 2Ag + HCOO^{-2} + 2H_2O \quad [3]$$

Improving the structure of the starting silver-tin oxide composite powder is essential to obtain the proper mechanical and electrical properties of the silver-tin oxide compacts and especially for a full density in the final sintered products. Factorial-designed experiments were used to identify optimal plating bath conditions.

From the experimental data, the optimal conditions for the electroless silver plating on the tin oxide colloidal particles were identified as follows:

- Bath temperature, 50 °C
- Concentration of silver nitrate, 0.69*M*
- Concentration of formaldehyde, 1.5*M*
- Silver ion feed rate, 20.7 mmole/min
- pH, 9.5

This condition produced separated powders without any agglomeration. It also yielded a uniform powder size distribution, which was 1.5 μm in diameter, as shown in Fig. 3. By the energy dispersive analysis of the X-ray, there were apparently no exposed tin oxide in every case. Also, the X-ray diffraction lines were obtained only from the silver. The silver on the silver-tin oxide composite powders was examined by X-ray line broadening to determine their crystallite size. It was determined that the silver crystallite size was 0.047 μm in diameter.

3.3 *Development of a Powder Metallurgy Process for Consolidation of Silver-Tin Oxide Composite Powders*

During compaction of these composite powders, increasing pressure provided better packing and led to decreasing porosity. High pressure increased density by contact enlargement through plastic deformation. Thus, the pressure caused localized deformation at contact, causing work hardening, and allowing new contacts to form as the distance between powders decreased. During deformation, cold welding at the interparticle contacts contributed to the development of strength for the compact.

During the initial stage of sintering, the silver-tin oxide composite powders form bonds with rapid neck growth. The local curvature gradient in the neck region provides the initial driving force, as noted by Thummer and Thomma.[14] At longer

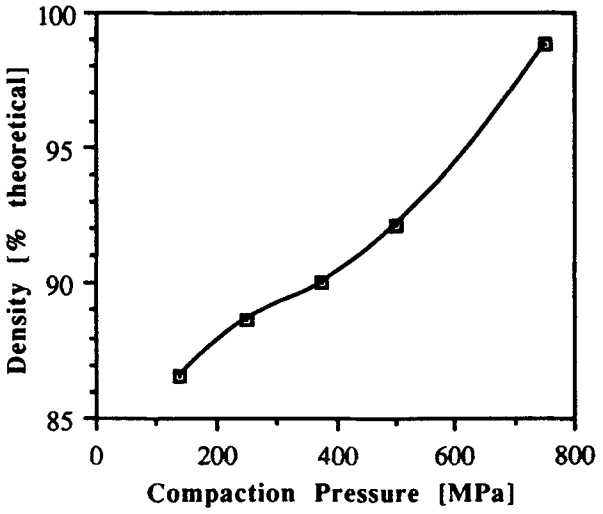

Fig. 4 Effect of compact pressure on the density of silver-15 vol.% tin oxide composite (sintering temperature, 850 °C).

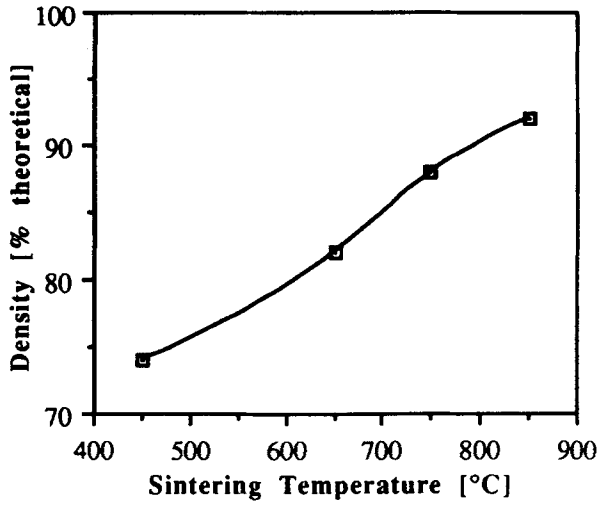

Fig. 5 Effect of sintering temperature on the density of silver-15 vol.% tin oxide composite (compaction pressure, 750 MPa).

sintering times, the pore structure becomes smoothed, eliminating the major curvature gradients. Grain growth usually occurs along with pore shrinkage during the later stages of sintering.

It was found that sintering temperature was the most important factor in obtaining a fully dense silver-tin oxide electrical contact material. Higher compaction pressures were also found to produce higher densities. The sintering time did not seem to have a significant influence on the density. However, the longer sintering times will typically improve the degree of sintering if grain growth occurs. Because this experiment dealt with fine powders, 1.5 μm in diameter, faster neck growth is expected so that less sintering time is needed, or alternatively, one needs a lower sintering temperature to achieve an equivalent degree of sintering. Additionally, it was performed in an air atmosphere to achieve the removal of the captured reducing agent by burning at the initial stage of sintering. Consequently, neutral atmospheres were not used.

From the experimental data obtained, optimal conditions for consolidating silver-tin oxide composite powders would be as follows:

- Compaction pressure, 750 MPa
- Sintering temperature, 850 °C
- Sintering time, 3 hr
- Heating rate, 8 °C/min
- Sintering atmosphere, air

Figure 4 shows the effect of compaction pressure on the sintered density when other consolidating conditions are the same as the optimal conditions. As shown in this plot, compaction pressure is a major factor in obtaining a fully dense material. It was found that at least 500 MPa of compact pressure was needed to reach densities higher than 90% of theoretical.

The effect of sintering temperature is shown in Fig. 5, which illustrates that the highest density obtained by sintering prior to repressing was 93.6% of theoretical. To increase density after sintering, some secondary working was carried out on the sintered pellet. Mishima and Sugita[11] had success in increasing density by repressing of sintered silver-oxide contact material. In the present study, repressing of the pellet followed by resintering increased the density up to 98.9%.

3.4 *Evaluation of Silver-Tin Oxide Electrical Contacts*

To evaluate the ductility of the composite and determine the volume loading limit of tin oxide, the sintered pellets were cold rolled. The pellets were rolled until cracks appeared. An end point was determined by the first appearance of cracks. Figure 6 shows the reduction in thickness of sintered composite after cold rolling as a function of volume loading of tin oxide.

Tin oxide volume loading of 15% is common in commercial electrical materials, which is produced by blending and consolidating silver powder with tin oxide or cadmium oxide powder. It has been reported that these materials could be cold rolled to 25%. The contact composite of silver-15 vol.% tin oxide electrical contact developed here, however, can undergo 30% reduction in thickness by cold rolling and has a density of at least 99% of theoretical. It is likely that this composite would be ductile enough for service even at 20% volume loading of tin oxide.

It was found that the ductility of silver-tin oxide had a close relationship with microstructural and compositional changes. The density decreased as the volume loading of tin oxide increased. Discrete spherical tin oxide particles yielded more ductile solids than aggregated particles. Silver-tin oxide composites with dense, spherical tin oxide particles were more ductile than silver-tin oxide composites made from clusters of tin oxide in which the tin oxide appeared as grape clusters.

Hardness in silver-tin oxide composites is affected by the microstructure, volume loading of tin oxide, and particle size. Figure 7 shows how the volume loading of oxide affects the hardness. It also shows the effect of secondary working after sintering, which provided the microstructural changes in porosities and grain sizes of the composites. Because large amounts of tin oxide particles were dispersed in silver-15 vol.% tin oxide, the hardness is much higher than that of silver-2

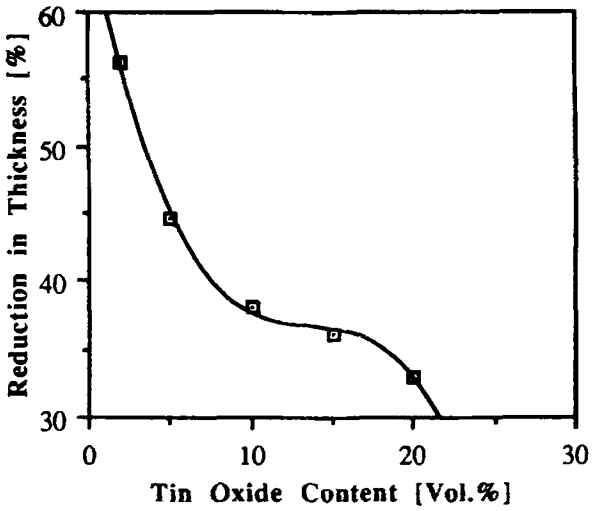

Fig. 6 Reduction in thickness on cold rolling before crack appearance showing the effect of volume loading of tin oxide.

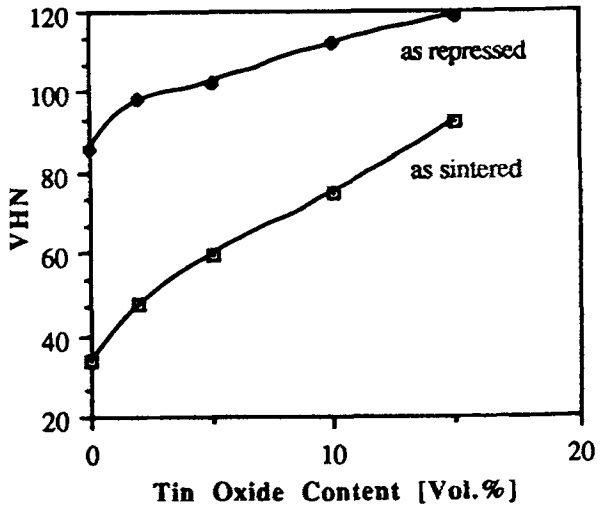

Fig. 7 Hardness as sintered and as cold rolled at different tin oxide volume loading.

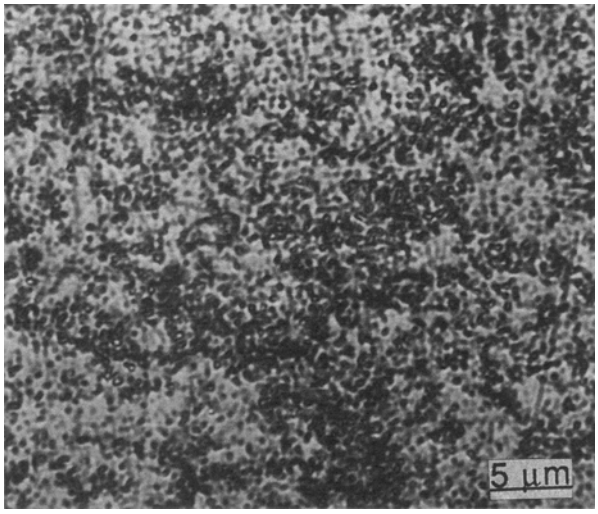

Fig. 8 Optical micrograph showing microstructure of sintered silver-15 vol.% tin oxide (cold rolled 90% in thickness).

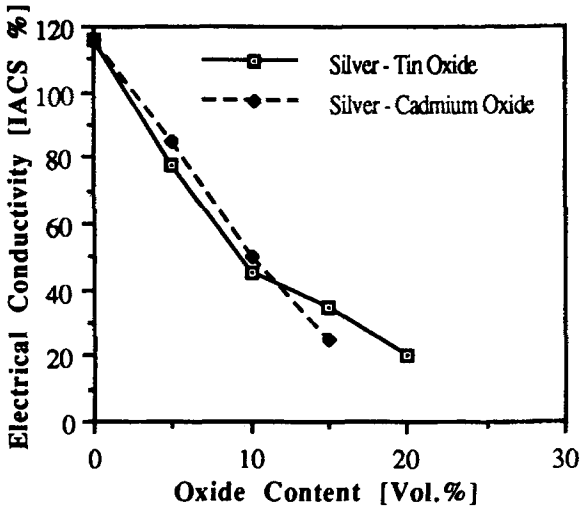

Fig. 9 Electrical conductivity of silver-tin oxide composites compared with silver-cadmium oxide electrical contact materials (IACS: International Annealed Copper Standard, 17.24 µ Ω = 100% at 20 °C).

vol.% tin oxide. The hardest state is obtained after repressing and strain hardening. The softest state is after sintering, but before cold working.

Microstructural studies showed that the tin oxide particles were well dispersed in the silver matrix. Figure 8 shows the tin oxide dispersion in this sintered composite. No stringers of tin oxide particles developed, even after cold rolling of 90%. The microstructure of a silver-tin oxide composite can be controlled when the powders used to make the composites are prepared by electroless silver plating on tin oxide particles. In this process, it is possible to control the particle size of the tin oxide, its shape, and the degree of tin oxide particle aggregation. In addition, one can control the volume loading of the tin oxide. These well-dispersed tin oxide particles would serve to increase the arc welding resistance for contact points in protective switches and circuit breakers and would not grow in needlelike crystals on thermal aging because they are separated from each other. Hardness would be high enough for sufficient wear resistance due to the dispersion of the hard oxide particles.

The electrical conductivity of the compacts was measured and is shown in Fig. 9. As might be expected, conductivity is related to volume loading of the tin oxide. It was also found that these composites had electrical conductivities as good as silver-cadmium oxide electrical contact materials.

4 Conclusions

As a result of this investigation the following conclusions can be deduced. The microstructures of silver-tin oxide composites dramatically depend on the uniformity of distribution of the tin oxide in the silver. The most uniform distribution that can be obtained is one in which the tin oxide particles are plated with a dense, uniform layer of the silver. The individual dense coating can be produced by an electroless plating process. This is done by introducing a soluble salt (silver nitrate) and reducing agent (formaldehyde) into a dilute solution of the colloidal tin oxide aquasol.

Optimal conditions were defined for producing fine and uniform powders without agglomeration. For consolidating the powders to a fully dense silver-tin oxide electrical contact material, optimal powder metallurgy conditions were also defined. The ductility of silver-tin oxide composites is important for electrical contact uses. Silver with 15 vol.% tin oxide prepared in this manner has a high enough ductility to be formed into shapes that can be used as electrical contacts.

Tin oxide is now being used as a replacement for cadmium oxide, which is toxic. The electroless plating process enables control of the amount of tin oxide desired in the composite. The power metallurgy preparation of silver-tin oxide electrical contacts from these electroless plated composite powders is a process that can improve the conventional processes by the internal oxidation of silver-tin alloys or a powder metallurgy approach consisting of mixing tin oxide with silver powders followed by consolidation.

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