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Electroless silver plating of oxide particles in aqueous solution

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It has been demonstrated that silver could be plated on colloidal oxides by reducing silver salts in the presence of colloidal oxides in aqueous solution. In this electroless plating manner, silver coatings have been applied to colloidal silica, tin oxide and to these colloids which have previously been coated with a few monolayers of tin silicate. Data from this study have demonstrated the technical feasibility of electroless plating for the preparation of silver–tin oxide composites as a source of this material for electrical contact materials.

1. Introduction

The production of colloidal sols for various purposes such as use in glass and ceramic processing, study of the basic properties of nucleation and growth of sols, and utilization in disperse systems, has long been of interest to scientists and engineers. Applications for their use as dispersants in metal systems have also been attractive, because they can provide stronger alloys as well as restricting recrystallization and grain growth in them. Some examples are dispersion-hardened nickel/thoria [1] and grain-growth inhibited tungsten/thoria filaments for electric light bulbs.

For some time silver contacts for electrical switching have contained cadmium oxide additions for the purpose of preventing arc erosion of the contacts during opening and closing the circuit. Owing to the fact that vaporization of cadmium oxide during switching was detrimental to workers' health, the use of cadmium oxide in contacts has been banned by health organizations. To replace the cadmium oxide, many foreign companies have utilized tin oxide in the silver electrical contacts [2, 3]. Two methods have been used to provide a mix of tin oxide particles in the silver. One method, followed by German companies, is by internal oxidation of a silver–tin alloy [4]. 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 [5]. Each of these methods has drawbacks in the successful production of silver/tin oxide compacts. In the internal oxidation process, the tin oxide produced provides a surface barrier to further oxidation in alloys containing more than about a 10% tin alloy. In the powder metallurgy process, the tin oxide particles grow in a needle-like morphology during the sintering process and produce a highly brittle product [6].

One approach to the solution of the problem of producing silver/tin oxide compacts of good ductility would be to produce a tin oxide sol and completely coat the sol with silver in an electroless plating process. The particles could then be separated from solution, pressed and sintered to produce a ductile silver/tin oxide compact. This paper describes the methods which have been developed to plate tin oxide sols and silica sols coated with monolayers of tin oxide or tin silicate with silver in aqueous solutions.

2. Experimental procedure and results

2.1. Preparation of tin oxide sols

A tin oxide sol was prepared in the following manner: a 0.1 M solution of sodium metastannate was prepared by dissolving 8 g $Na_2SnO_33H_2O$. While holding at a temperature of 90 °C, the solution was neutralized over a 6 h period by adding, at a uniform rate, a solution of 0.2 M HNO_3. The product was a milky white sol having no tin oxide aggregates. When an aged sodium metastannate solution was used, or when concentrated sodium metastannate solutions were used, a considerable number of tin oxide particles was produced which settled to the container bottom. The sol particles produced were found to be porous particles of 0.03 μm diameter. The porous tin oxide was composed of fine particles, 5–8 nm diameter (Fig. 1).

To prepare tin oxide sols by grinding techniques, reagent-grade tin oxide powder was ball-milled in an ammoniacal solution. 20 g tin oxide was placed in 200 ml deionized water containing 3 ml concentrated ammonia. The mixture was placed in a polyethylene bottle containing 300 g, 5 mm diameter, stainless steel balls and rotated for 12 h. The product obtained is shown in the electron micrograph in Fig. 2.

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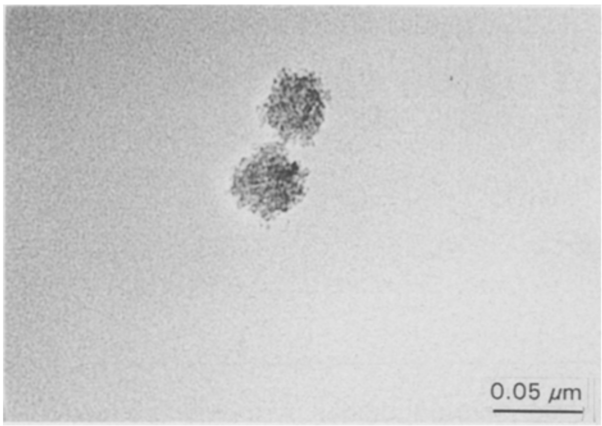

Figure 1 Transmission electron micrograph of polymerized tin oxide particles.

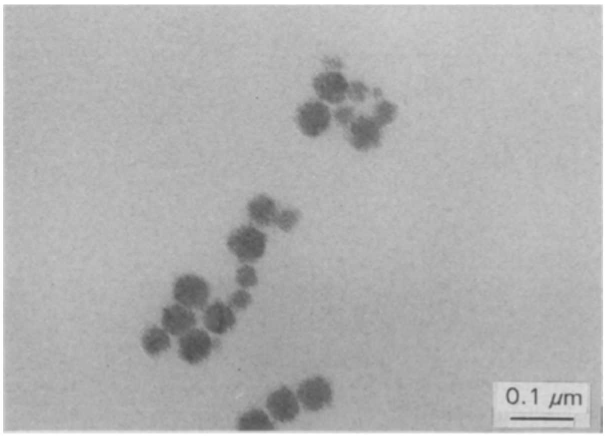

Figure 2 Transmission electron micrograph picture of tin oxide particles prepared by grinding technique.

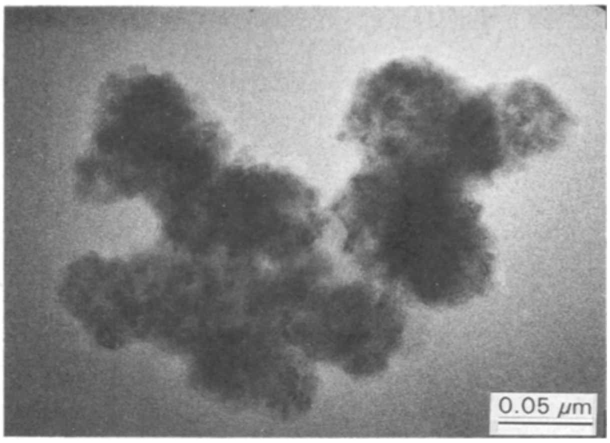

Figure 3 Transmission electron micrograph of hydrothermally grown tin oxide particles.

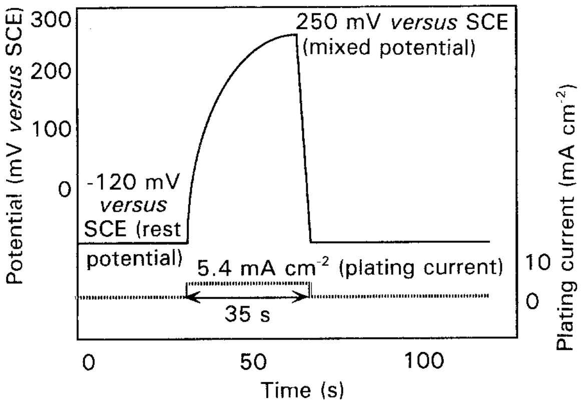

Figure 4 Imposed current pulse and potential response used for coulostatic monitoring of electroless silver plating rate.

2.2. Hydrothermal growth of tin oxide particles

In order to grow tin oxide sol particles to a larger size, tin oxide sol particles were treated in an autoclave at 290 °C. The sols were sealed in Pyrex tubes and heated for 24 h in an autoclave. Particle rearrangement occurred such that 100 nm size particles were produced which were not totally dense. A photograph of the particles produced is shown in Fig. 3.

2.3. Electroless plating of silver on the tin oxide colloids

A reducing agent (generally formaldehyde) and a silver solution (silver nitrate) were separately fed into the tin oxide aquasol. Initially the rate of change of EMF of the solution was monitored using a Princeton Model 173 potentiostat with silver as a working electrode, saturated calomel electrode as a reference and graphite as a counter electrode. The rest potential of 0.5 M CH_2O solution was − 120 mV versus the standard calomel electrode. Upon addition of 0.25 M silver nitrate the potential rose to about 250 mV. Colloids of 100 nm size were used. Reagents were added through capillary tubes at points of vigorous agitation so that the ions in the feed solutions were diluted before the colloidal tin oxide particles could gel. Within 100 s the reaction was completed and the potential fell to − 120 mV. Fig. 4 shows a typical reaction curve. Within the limits of experimental error, the length of the induction period was independent of whether or not there were nuclei present.

In all of the experiments conducted the pH was kept in the range 8–10, the temperature was varied from 20–60 °C and the concentration of the reagents varied from 0.2–0.5 M. The feed rate of silver nitrate varied from 1–30 mmol $min^{-1} g^{-1}$ of 100 nm size oxide particles to be treated. The results of the experiments conducted are shown in Table I.

The evidence of the presence of silver ions in the plating bath after the reactants had been added in runs at 21 °C indicated that at this temperature the reaction was too slow to precipitate the silver completely on the colloid. Cases of incomplete reaction occurred at 35 °C when the feed rate was increased to 9 and 27 mmol Ag $min^{-1} g^{-1}$ tin oxide. At 50 °C, a feed concentration of 0.2 M silver nitrate and a feed rate of 3 mmol Ag min^{-1}, experiments were run at pH values of 8 and 10 with no differences in the products observed. Above pH 10 the deposition becomes nonuniform and the silver spheres become hollow.

Various surfaces were prepared for the electroless deposition of silver. These included unmodified silica,

TABLE I Effects of feed concentration, feed rate and bath temperature on the electroless plating of silver on 100 nm tin oxide colloid

(vol %) SnO_2	Temp. (°C)	FC ($mmol\,l^{-1}$)	FR ($mmol\,Ag\,min^{-1}\,g^{-1}\,SnO_2$)	Observations
50	21	180	3	AgCl ppt on addition of HCl to bath
50	35	180	1	Very fine ppt, solution cloudy
50	35	180	3	Solution colourless, no AgCl ppt
50	35	540	9	AgCl ppt
50	35	540	27	AgCl ppt
50	37	180	3	Final solution tan but no ppt
50	50	180	3	Solution colourless, no AgCl ppt
50	52	180	3	Solution colourless, no AgCl ppt
25	50	60	12	Solution colourless, no AgCl ppt

TABLE II The effect of substrates on the deposition of electroless silver

No.	Oxide used	Oxide size (μm)	Product size (μm)
1	Tin oxide (peptized powder)	0.1	0.8–1.5
2	Tin oxide (polymerized)	0.1	0.5
3	Silica (unmodified)	0.1	0.4–4
4	Tin silicate-coated silica (10 monolayers)	0.1	0.1
5	Tin oxide-coated silica (1 monolayer)	0.1	0.4
6	Tin oxide/tin silicate/silica		
	2 monolayers of each	0.1	0.3
	10 and 25 monolayers of each	0.1	0.1

unmodified tin oxide, silica coated with 2 and 10 monolayers of tin silicate, silica with a coating of one monolayer of tin oxide and silica with a coating of 10 monolayers of tin silicate upon which was coated 5 or 25 monolayers of tin oxide. The initial and final particle size of the colloid particles was determined by TEM. The coated particles were also examined in the SEM to determine whether or not they were completely coated with silver. Table II is a compilation of the results of these experiments. Fig. 5 shows the morphology and the appearance of the Ag/SnO_2 powder which had been electrolessly plated on peptized tin oxide particles.

It was found that when the silica and tin oxide are silver plated, large particles are produced which indicates aggregation of the colloidal particles. The products obtained in both cases consist of two distinct size fractions. When as little as one monolayer of tin oxide is polymerized on the silica prior to silver plating there is much less aggregation of the ultimate particles. With a coating of tin silicate of 10 monolayers, aggregation of the ultimate particles is essentially eliminated. Also with an overlay of tin oxide on tin silicate on silica there is little or no aggregation of the colloid. In no case was any exposed or unplated oxide found in the product.

Another series of experiments was performed to determine the effects of feed rates and feed concentration of silver. A silica colloid coated with tin silicate and tin oxide was used in the experiments. The results of this series of experiments is recorded in Table III.

Particles which are coated with 90 vol % silver should double in size. This was the result observed in Samples 1, 2, and 4. In Sample 3, aggregation of the particles appeared to occur, resulting in a larger particle size than that calculated. The difference between Samples 2 and 3 was the feed rate. In Sample 4, when the feed concentration was increased, aggregation no longer occurred. In both Samples 3 and 4, produced at high feed rates, the product was difficult to filter. The product in Sample 4 appeared to be a silver sol.

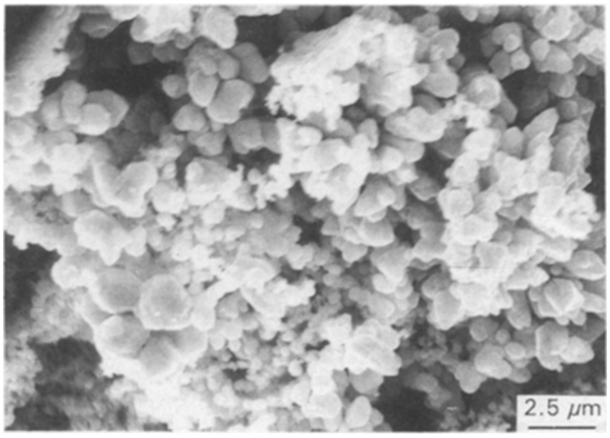

Figure 5 Morphology of electrolessly plated silver-tin oxide composite powders.

3. Discussion

It was found that tin oxide polymerizes at a higher pH than silica, the charge on the particles is less, the

TABLE III The effect of feed concentration and feed rates on final powder size and filterability. Solutions all contained 10 vol % oxide and were held at 50 °C. Original particle size = 80 nm

No.	FC (mmol Ag l^{-1})	FR (mmol Ag min^{-1} g^{-1} oxide)	Powder size	Filterability
1	230	2.1	150 nm	good
2	230	6.3	150 nm	good
3	230	19	750 nm	poor
4	690	19	150 nm	poor

growth process is slower, and gel rearrangement does not occur at 90 °C as it does for silica sols.

In aqueous systems, tin oxide nuclei (5–8 nm diameter) can be formed by the reaction of sodium stannate with acid. However, these nuclei have a strong tendency to aggregate. At temperatures of 100 °C, growth of these nuclei by accretion was not successful. When tin oxide aquasols are hydrothermally treated up to 290 °C in pressure autoclaves, gel rearrangement occurs but dense particles are not formed.

From the experiments it is evident that tin silicate can be deposited as a dense coating on 100 nm silica particles and that this coating can be overcoated with a dense coating of tin oxide. Tin oxide powders can be deagglomerated by milling and these deagglomerated particles can be stabilized by treating them with aqueous ammonia. The particles are stabilized by adsorption of the negative hydroxyl ion.

Preparation of tin oxide sols plated electrolessly with silver has been shown to be feasible under the right conditions of pH, temperature and feed concentration. In order to prevent aggregation of the sol particles during the plating process, concentration of the reagents and the method of mixing were selected in such a manner as to limit this process. This involved using dilute solutions and maximum agitation during the plating process. The charge on the sol particle could be affected by pH and by the nature of the surface of the colloidal particles. It was found that the larger the particles, the less likely they are to aggregate. The potential obtained during the electroless plating of silver on the sol particles is a mixed potential, and is the potential obtained as a result of the cathodic and anodic reactions occurring at the sol particle surface

$$2Ag^+ + 2e^- \rightarrow 2Ag \qquad (1)$$

$$CH_2O + 3OH^- \rightarrow HCOO^- + 2H_2O + 2e^- \qquad (2)$$

4. Conclusion

Two methods of preparation of tin oxide aquasols have been described. The methods include preparation by precipitation from solution and mechanical grinding. The sol particles were characterized by electron microscope measurement of their size. Also the sol particles were able to be grown to a larger size by pressure autoclaving. A method was developed to coat silica and tin oxide particles with several monolayers of tin oxide and tin silicate. These particles were then electroless plated with silver metal in the presence of a reducing agent. Silver-plated tin oxide and silica particles were found to aggregate. This aggregation was essentially eliminated by coatings of 10 monolayers of tin silicate or with overlays of tin oxide on tin silicate.

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