

The Production of Palladium Powders for Electronic Applications

REACTION CONDITIONS DETERMINE SURFACE CHARACTER

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Recent investigations into metal powder fabrication by chemical precipitation techniques have shown that a wide variety of powder morphologies can be obtained by making subtle changes in the reaction parameters. Palladium powders produced using these techniques find wide application in the microelectronics industry, particularly as metallisations for multilayer ceramic capacitors or in thick film interconnection systems.

The microelectronics industry requires metal powders for incorporation into thick film inks or pastes, and the technology of thick film materials and their application to microelectronics has been extensively reviewed (1-6). The major uses of such inks occur during the manufacture of hybrid integrated circuits where they are screen-printed and then fired to form the conducting layers of the interconnection system or to form the internal electrodes of multilayer ceramic capacitors (MLCCs).

The properties of the metallic components of thick film inks intended for the internal electrodes of MLCCs are extremely important as compatibility is required between the metal powder and the organic medium of an ink, and between the ink itself and the surrounding dielectric material of the MLCC. The most widely used metals for this application are palladium or palladium-silver composites.

Historically, metal powders prepared by the chemical reduction of simple metal salts were used in the manufacture of MLCCs. However, such powders were often extremely fine with particle diameters of 0.001 to 0.1 μm , they exhibited a high surface area ($>10\text{m}^2/\text{g}$) and as a result were often catalytically active or even pyrophoric. Consequently they were of only limited use when combined with an organic

medium to form screen printable thick film inks. They suffered from three very serious disadvantages, in particular:

[i] High surface area powders require excess organic medium for adequate wetting of the powder during paste fabrication, and this can have a detrimental effect on the final rheology. The high oxide content associated with such powders can promote excessive gelling of the ink and screen printing may therefore become difficult.

[ii] During the firing stages, the fine material can interact catalytically with the organic medium of the ink creating hot spots inside the assemblies and leading to rapid vapour release, blistering and delamination of the capacitors as they are formed.

[iii] During the latter stages of firing, the metal powder sinters and shrinks. The shrinkage characteristics of very fine metal powders are usually excessive and unlikely to match that of the surrounding dielectric material. Consequently, tiny "islands" of metal are formed which result in discontinuous metal patterns of poor conductivity. Shrinkage incompatibility can also lead to delamination.

Thus it was considered necessary to produce relatively non-active metal powders which would be fine enough to be used in thick film pastes but of sufficiently low surface area to

inhibit catalytic activity. On firing, such materials should also possess shrinkage compatible with the surrounding dielectric in order to form smooth, high density metallisations. Therefore there was a requirement for a range of powder types of varying morphology, surface area and tap density, depending upon the organic medium chosen to make the ink and the dielectric selected for the MLCC.

Recent investigations at the Johnson Matthey Technology Centre have been concerned with the fabrication of suitable metal powders for such applications. The method adopted was derived from electroless plating techniques, with metal salts and complexes in an aqueous medium being precipitated to the metal by the action of a chemical reducing agent.

Studies reported in the literature (7, 8, 9) have led to the general observation that precipitation is a combination of a number of stages, namely: nucleation, where solid phase particles are formed out of a liquid phase; growth, where solid material grows around the original nuclei; and agglomeration where the particles collide and combine. A supersaturated solution is, of course, one which contains more solute than that indicated by the equilibrium solubility or saturation point, and is a prerequisite for the growth mechanism to take place; while nucleation, which may be promoted by the presence of impurity substrates, requires even higher levels of saturation. However, when the precipitation of metals by the chemical reduction of metal ions from aqueous solution is under consideration, concepts such as saturation, supersaturation, nucleation and growth become less certain in view of the vanishingly small solubility of metals in water, and there appears to be very little published in the literature about this form of precipitation.

The investigations made at these laboratories have shown that although the basic reaction remained the same, which in the case of palladium is $\text{Pd}^{2+} + 2\text{e} \rightarrow \text{Pd}^0$, subtle variations in the reaction parameters can have a remarkable effect on the physical characteristics of the

metal powder formed. For this purpose important variables include the concentration of the reactant or the reducing agent, the form of the metal salt or complex, the choice of the reducing agent, the reaction temperature, the mode and degree of agitation of the solution, the solution viscosity and the presence of additives or polyelectrolyte surfactants

Surface Morphology of the Powders

The results of this work are illustrated by the scanning electron micrographs which show a variety of palladium powders, all at similar magnifications. A very fine, high surface area ($>10\text{m}^2/\text{g}$) material which, for the reasons outlined earlier, is of little use in MLCC applications, is shown in Figure 1. Figure 2 illustrates a nodular powder having a lower surface area (1 to $2\text{m}^2/\text{g}$); however, the surface irregularity and wide particle size distribution promotes uneven sintering during the firing stages and this leads to poorly defined conducting layers. Figure 3 shows a dendritic material which displays surprisingly good sintering characteristics which are considered to be due to the formation of a mat-type structure during printing. This same factor, however, can result in screen blockage which makes the powder of little direct use. A powder composed of spherical particles is shown in Figure 4; again the high level of agglomeration would result in poor as-fired properties. Figures 5 and 6 illustrate powders consisting of spherical particles but here there is less agglomeration. This is the type of powder most useful for MLCC fabrication, the smoother surfaced material possessing superior sintering properties.

Subtle alterations to precipitation parameters can also be used to control particle size and agglomeration, as shown in Figures 6, 7 and 8. Consequently surface area, tap density, Scott Density and Fischer Sub Sieve Size can also be regulated. The powder illustrated in Figure 8 has a particularly low particle size ($\approx 0.1 \mu\text{m}$ diameter) that facilitates printing of a buried electrode to a minimal thickness, but which retains a coherent structure. The use of this type of powder is expected to increase in the

Fig. 1 This very fine, high surface area type of powder, often referred to as a "black" because of its very dark appearance, is of little use in microelectronic applications



Fig. 2 Although having a lower surface area than the powder in Figure 1, this nodular powder has a wide particle size distribution and suffers from uneven sintering during firing leading to discontinuous metal layers

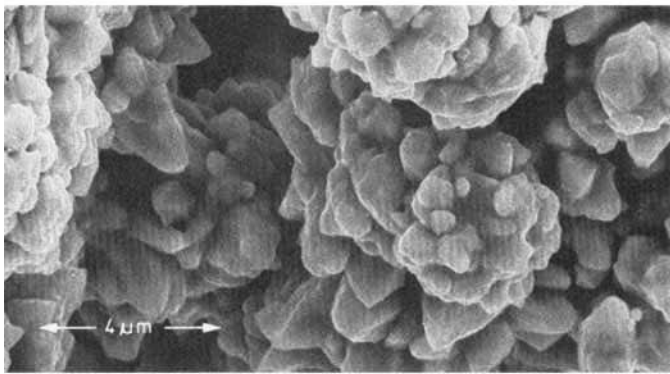


Fig. 3 Dendritic powders such as this form a mat structure on screen printing leading to strong, coherent fired layers. However, a tendency for screen blockage to occur during printing makes powders such as these of limited practical use

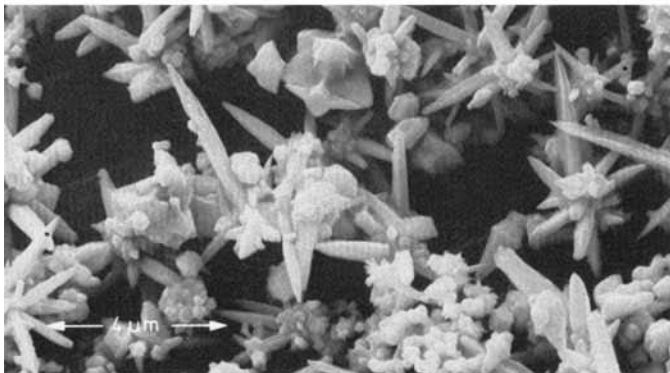


Fig. 4 This powder is composed of large, semi-nodular, uneven spheres. The high level of agglomeration does not promote satisfactory sintering characteristics, and can lead to porosity in the fired films

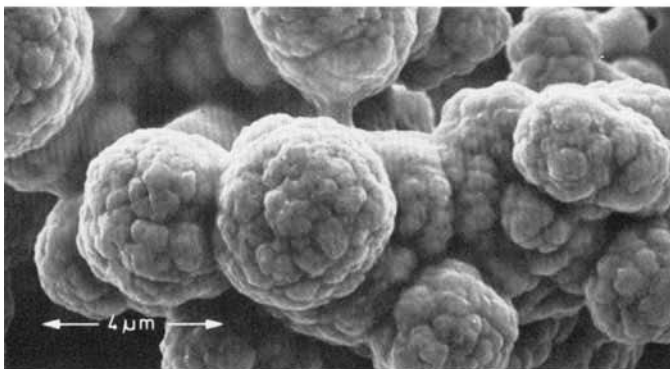




Fig. 5 This powder consists of spherical particles with lower agglomeration than the powder shown in Figure 4, but it has a considerable degree of surface roughness. Although an improvement over previously illustrated material, it remains unsatisfactory for MLCC applications

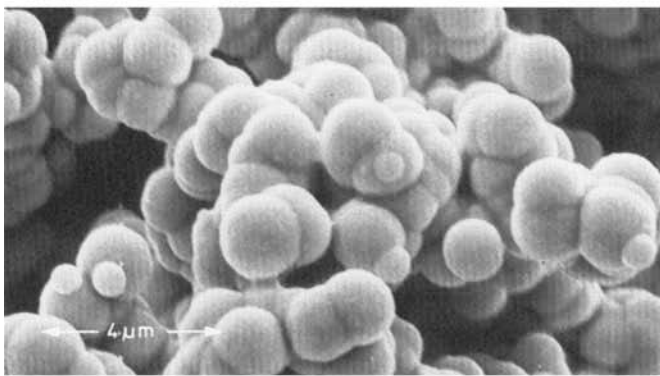


Fig. 6 Composed of 0.5 to 2 microns diameter smooth spheres of low agglomeration, this material approaches that currently preferred for MLCC applications. The variations in particle size and agglomeration achieved by subtle changes in precipitation parameters can be seen by comparing Figures 6, 7 and 8

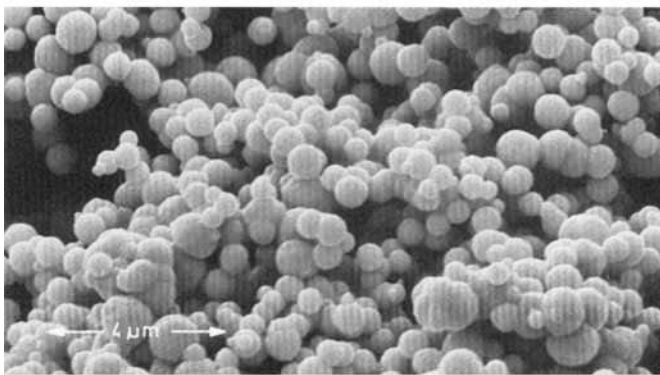


Fig. 7 This material which is made up of smaller spheres 0.2 to 0.5 microns in diameter has lower agglomeration and exhibits the desirable sintering and shrinkage properties required for MLCC manufacture

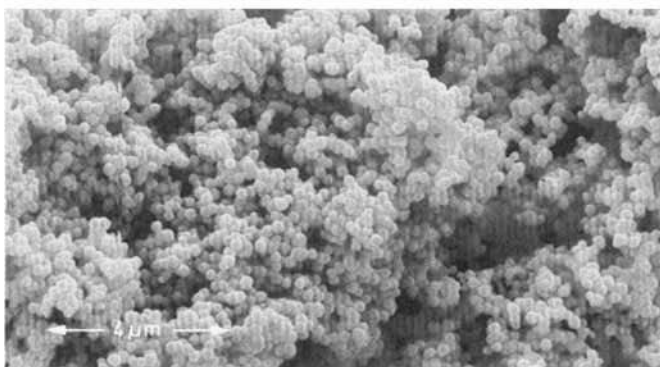


Fig. 8 Powder composed of very small spheres approximately 0.1 microns in diameter and exhibiting minimal agglomeration not only retains an acceptably low surface area to form high quality screen printing pastes but also allows the fabrication of extremely thin internal electrode layers, thus offering substantial savings in metal costs

near future as it offers economic advantages.

The assessment of a metal powder for a particular application requires further characterisation in addition to measurements of surface area, tap density and particle size distribution. The determination of oxide layers or the presence of surface contaminants which may interact harmfully with any dielectric material requires the use of X-ray Photoelectron Spectroscopy. Transmission Electron Microscopy and X-ray Diffraction are used for the determination of fundamental crystallite size, which incidentally provides information on the particle growth mechanism. The presence of bulk impurities which can drastically alter MLCC performance is determined by X-ray Fluorescence Spectroscopy, in addition to the traditional methods of chemical analysis. Finally, Simultaneous Thermal Analysis and Dilatometry are used to examine sintering and shrinkage behaviour.

The investigations carried out at the Johnson Matthey Technology Centre have involved mainly palladium and silver-palladium, reflecting the importance of the platinum group metals in the manufacture of MLCC electrodes. This work has provided a better understanding of the fundamental aspects of precipitation of

these metal powders, which can also be utilised for other applications such as improved MLCC end terminations and hybrid interconnect metallisations. The electronics industry requires and demands high purity powders of advanced formulation for existing and predicted future applications; it is knowledge gained from investigations such as these recorded here that will enable the constantly changing needs of this important industry to be satisfied.

References

- 1 J. R. Larry, R. M. Rosenberg and R. O. Uhler, *IEEE Trans., Components, Hybrids Manuf. Technol.*, 1980, **3**, (2), 211
- 2 B. Walton, *Radio Electron. Eng.*, 1975, **45**, (3), 139
- 3 T. H. Lemon, *Platinum Metals Rev.*, 1975, **19**, (4), 146
- 4 G. Fisher, *Ceram. Ind.*, April 1983, **120**, (4), 80
- 5 K. E. G. Pitt, "An Introduction to Thick Film Component Technology", Mackintosh Publications, Luton, 1981
- 6 N. M. Davey and R. J. Seymour, *Platinum Metals Rev.*, 1985, **29**, (1), 2
- 7 A. G. Walton, "Principles of Precipitation of Fine Particles", Chapter 5 in "Dispersions of Powders in Liquids", ed. G. D. Parfitt, Applied Science Publishers, London, 1973
- 8 J. Garside, *Chem. Ind. (London)*, 1983, (13), 509
- 9 J. Hecklen, "Colloid Formation and Growth", Academic Press, New York, 1976

Oxygen Probe for Heat-Treatment Furnaces

In earlier times steel was heat-treated by craftsmen who depended largely upon their accumulated knowledge to ensure that the properties of the metal matched the application. Present day requirements demand more exact control, not only of temperatures but also of furnace atmospheres, for if the latter is chemically unsuitable the composition and hence the physical properties of the steel will be adversely affected.

To provide a reliable and accurate indication of available carbon in furnace gases Corning Glass Works, of Corning, New York, U.S.A., have now developed a solid state oxygen measuring probe. Somewhat similar probes find application in chemical process technology, and can assist in vehicle emission control.

The Corning Glass probe includes a yttria stabilised zirconia solid electrolyte and a platinum electrode which is exposed to the

furnace atmosphere. Oxygen molecules in the furnace are turned into ions by the catalytic effect of the platinum and are then conducted through the zirconia where they recombine into molecules, the electrical potential generated depending upon the difference in the amounts of oxygen inside and outside the furnace. The oxygen produced in the furnace is directly related to the concentration of carbon monoxide and carbon dioxide, and thus to the amount of carbon available for hardening steel by carburising and carbonitriding treatments.

Operating in the range 760 to 1100°C, the probe can be used with furnace atmospheres generated from natural gas, nitrogen+methanol mixtures and propane-derived gases.

In the U.K. the Corning Glass probe is marketed by Land Pyrometers, Dronfield, Sheffield S18 6DJ, from whom additional information is available.