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Properties of conductive films made from fine spherical silver–palladium alloy particles

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Silver–palladium alloy films were made by a thick-film technique using several metal powders prepared by the spray-pyrolysis method. Two types of powders were used: silver–palladium alloy powders (15 mol% Pd and 30 mol% Pd) and mixtures of silver and palladium powders. The fired films were about 2–3 μm in thickness. The alloy particles sintered uniformly in firing, whereas, in the case of the powder mixtures, the alloying of silver and palladium particles caused uneven particle growth and large voids were formed in the fired films. For this reason the films made from the alloy powders had better conductive properties than those made from the powder mixtures. The resistivities of the films made from the alloy powders were close to the intrinsic value for silver–palladium alloys. Further, the oxidation of palladium during heating in air was significantly suppressed in the alloy powders when the palladium content was lower than 30 mol% in accordance with thermodynamic considerations.

1. Introduction

In the manufacture of electronic devices such as hybrid integrated circuits and multilayer ceramic capacitors the technology of making conductive thick films from metal powders is of considerable importance. Precious metals (such as gold, silver, platinum and palladium), their mixtures or alloys, and cheaper metals such as copper and nickel are used for making the conductive films. Silver–palladium alloy films are very useful because of their stability, compositional flexibility, and relatively low cost. Metal powders for thick films have been mainly obtained through chemical precipitation from aqueous or organic solution of metal salts. This method can give the desirable particle shape and size at a low preparation cost. The fabrication of electronic devices having better capabilities, however, requires improved metal powders to prepare a conductive film. For example, in the precipitation method, it is difficult to prepare alloy powders and most silver–palladium alloy films have been made from mixtures of silver and palladium powders.

In our previous work [1–3], metal particles of silver, palladium, copper and silver–palladium alloy could be prepared by the spray-pyrolysis technique. These particles were fine (0.1–a few μm), spherical, well-crystallized, and free from aggregation. Silver powders prepared by this method gave very thin conductive films having low resistivity [4]. The purpose of this study is to characterize the fine spherical silver–palladium alloy particles prepared by the spray-pyrolysis technique as a raw material for the conductive film. Silver–palladium alloy films were prepared from two types of particles: silver–palladium alloy particles, and mixtures of silver and palladium particles. The properties such as texture and resistivity between the two types of films were compared.

2. Experimental procedure

2.1. Characterization of metal powders

An aqueous solution of palladium nitrate was prepared by dissolving palladium black in nitric acid. Palladium black was prepared from a palladium powder (99.9% pure; Rare Metallic Co., Ltd, Japan) by dissolving in aqua resia and precipitating by sodium formate (98% pure; WAKO Pure Chemical Industries, Ltd, Japan). The silver–palladium alloy powders used were prepared by the chemical flame method [2] from an aqueous solution of silver nitrate (99.8% pure; WAKO Pure Chemical Industries, Ltd, Japan) and the palladium nitrate. Powder X-ray diffraction using CuK_α radiation was used for determination of the powder composition by reference to the relation between the lattice parameter and the silver–palladium alloy composition [5]. The powders were examined for shape and size by a scanning electron microscope (SEM). The diameters of ca. 700 particles in the SEM photographs were measured to obtain the size distributions.

2.2. Preparation and analysis of silver–palladium alloy films

A paste was prepared by mixing the metal powder and an organic vehicle consisting of ethylcellulose and terpineol using a three-roll mill. No additives were used to reveal clearly the properties of the metal powders. The paste, consisting of equal weights of metal powder and the organic vehicle, was printed on to an alumina substrate (96% Al_2O_3, surface roughness ca. 1 μm; Kyocera Corporation, Japan) through a 200 mesh screen. The printed pattern (5 mm × 10 mm) was then dried at 150 °C in air. The dried film was fired for 10 min in air at temperatures ranging from 300 °C

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to 1000 °C at 100 °C intervals. Heating up to the firing temperature took 30 min, and cooling was done in 30 min.

The fired film composition was determined from the lattice parameters of the film on the alumina substrate; the film texture was observed by SEM; the film thickness was determined by metallographic observation of film cross-sections; and the electrical resistance (sheet resistance) of the film was measured using a digital multimeter (Model 3457A, Hewlett-Packard).

3. Results and discussion

3.1. Properties of metal powders prepared by the spray-pyrolysis technique

The following powders were prepared:

(1) powder No. 1: silver–palladium (15 mol %) alloy powder;

(2) powder No. 2: silver–palladium (30 mol %) alloy powder;

(3) powder No. 3: silver powder;

(4) powder No. 4: palladium powder.

No other phases were detected by X-ray diffraction. However, the diffraction lines of the alloy powders were slightly broader than those of the silver and palladium powders. This line broadening suggests that there is a little variation in composition within a particle and/or among particles. The particle shape of all the powders was spherical as shown in Fig. 1. Fig. 2 shows that the particle size distribution of the four powders is almost the same.

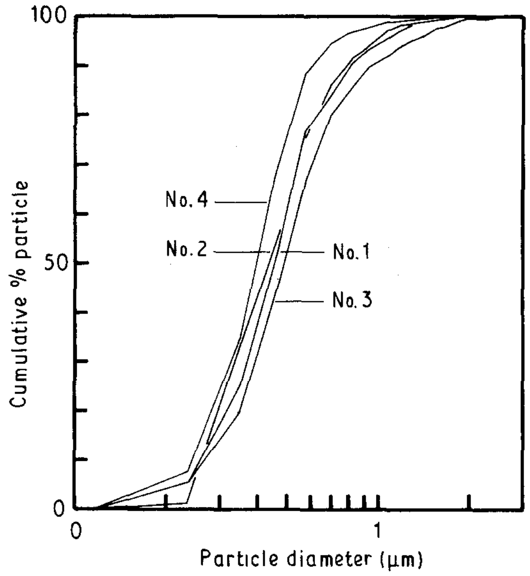

Figure 2 Particle size distributions of powders shown in Fig. 1.

3.2. The conductive properties of silver–palladium alloy films

The following films were made from the four powders given above:

(1) film A15: silver–palladium (15 mol %) alloy film made from powder No. 1;

(2) film A 30: silver–palladium (30 mol %) alloy film made from powder No. 2;

(3) film M15: silver–palladium (15 mol %) alloy film made from a mixture of powders No. 3 and No. 4;

(4) film M30: silver–palladium (30 mol %) alloy film made from a mixture of powders No. 3 and No. 4;

(5) film AG: silver film made from powder No. 3.

The electrical resistance of these films varied with firing temperature. Fig. 3 shows the texture of each film fired at the temperature where the resistance became the lowest. Films A15, A30 and AG were about 2 μm, and films M15 and M30 were about 3 μm in thickness. The black parts in the photographs are voids in the films. The voids in the films made from the alloy powders, films A15 and A30, were less than in those made from the powder mixtures, films M15 and M30. This may be the reason for the difference in

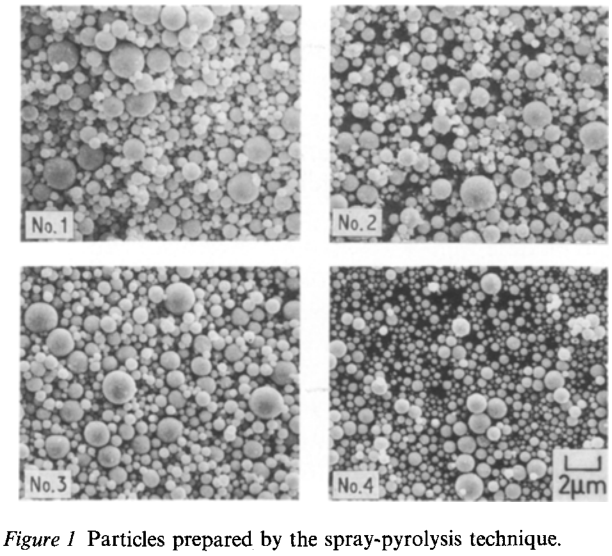

Figure 1 Particles prepared by the spray-pyrolysis technique.

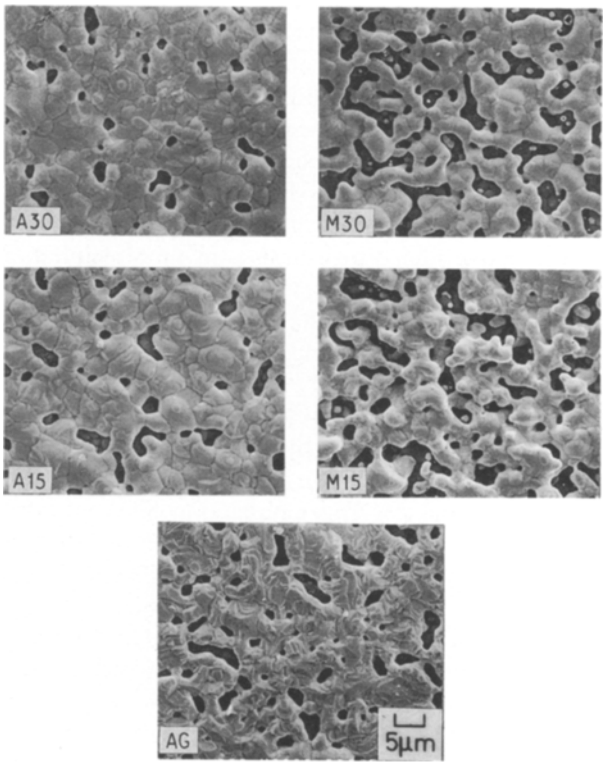

Figure 3 Textures of fired films. Firing temperature: (A30 and M30) 1000 °C, (A15 and M15) 900 °C, (AG) 800 °C.

electrical resistance between the two types of films as shown in Fig. 4. The resistivities of films made from the alloy powders were close to the intrinsic value for silver–palladium alloys [6]. Film AG also had good conductivity.

The texture change in films fired at low temperatures showed the different sintering behaviour between the two types of alloy films. Fig. 5 shows the textures of films A15, M15 and AG fired in the temperature range 300–600 °C. Films A30 and M30 showed structural change similar to films A15 and M15, respectively. Sintering of the alloy particles proceeds uniformly with increasing firing temperature as seen in film A15, whereas in film M15, the shapes of most of the particles become irregular at 400 °C and the irregular-shaped particles grow rapidly into large ones at 500 °C. Since it is suggested by the X-ray diffraction patterns shown in Fig. 6 that alloying of the silver and palladium particles proceeds in film M15 in the same temperature range, the shape change and rapid growth of the particles in film M15 are

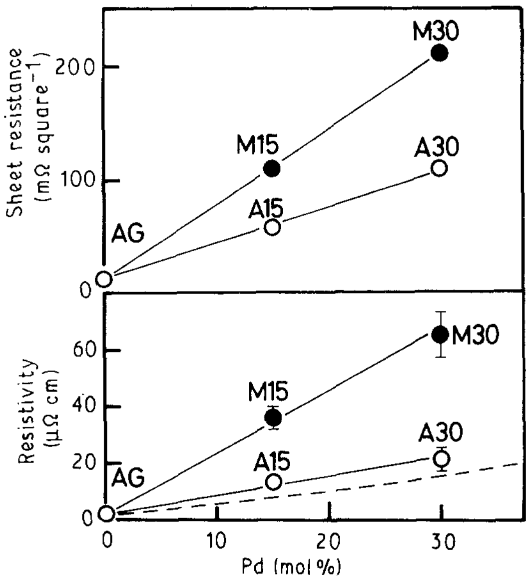

Figure 4 Electrical resistances of fired films shown in Fig. 3. The broken line indicates the intrinsic value for silver–palladium alloy [6].

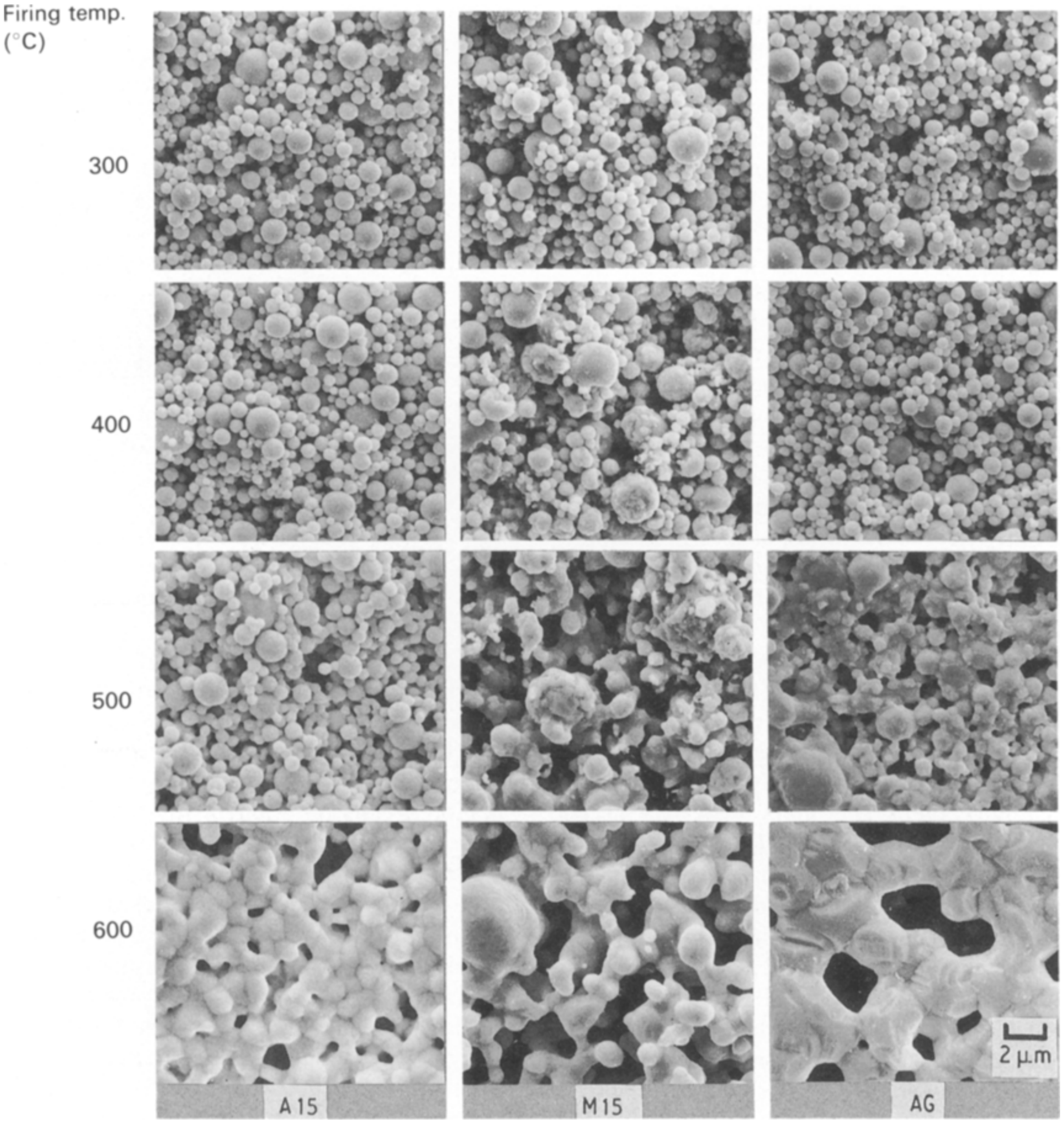

Figure 5 Texture changes in films A15, M15 and AG by firing at 300–600 °C.

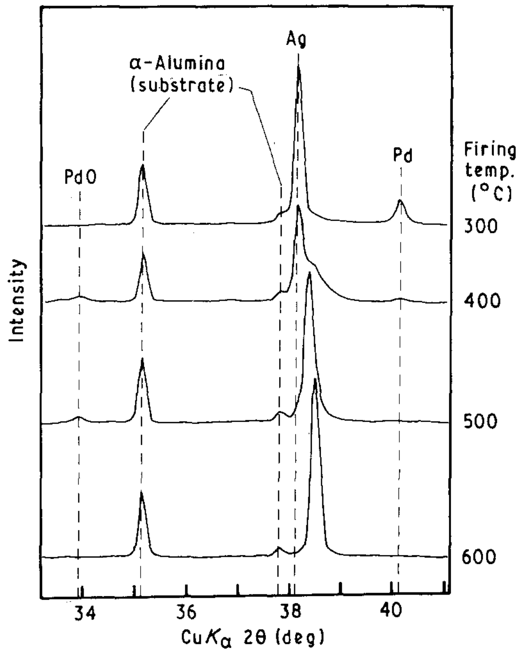

Figure 6 X-ray diffraction patterns of film M15 fired in the range 300–600 °C.

presumed to be the effects of the alloying. The alloying behaviour of silver and palladium was then investigated using an alloying model as follows. Palladium particles were dispersed on a silver plate and were heated. The structural change in the course of heating is shown in Fig. 7. Palladium particles change their shapes, and the small particles conglomerate into large particles after heating at 300 °C. Simultaneously, many cracks are formed in the silver plate around the palladium particles. These changes were not observed when the palladium powder and the silver plate were separately heated. After heating at 400 °C, irregular-shaped particles are formed on the silver plate whose surface becomes very rough owing to crack growth. The shape of the irregular-shaped particles is similar to that observed in film M15. This investigation indicates that the alloying between silver and palladium proceeds through the migration of silver, presumably because silver is much more mobile than palladium. From the findings, it is thought that the alloying in film M15 proceeds through silver migration towards palladium particles from surrounding silver particles and causes the uneven structure of the film. As a result, the large voids are formed in the fired films. Currently, several attempts have been made to get improved conductive silver–palladium thick films consisting of a low palladium content. They make use of very fine and dispersible palladium powders [7], organic palladium compounds [8], and silver–palladium composite (not alloy) particles prepared by palladium plating on silver particles, coprecipitation or mechanical alloying [9]. It is thought that the aim of all these attempts is the suppression of the uneven alloying reaction by making palladium components adjacent to silver particles as uniform as possible. From this point of view, the use of alloy particles is ideal, is simplest, and gives a good result; namely that the resistivities of the films obtained are close to the intrinsic value.

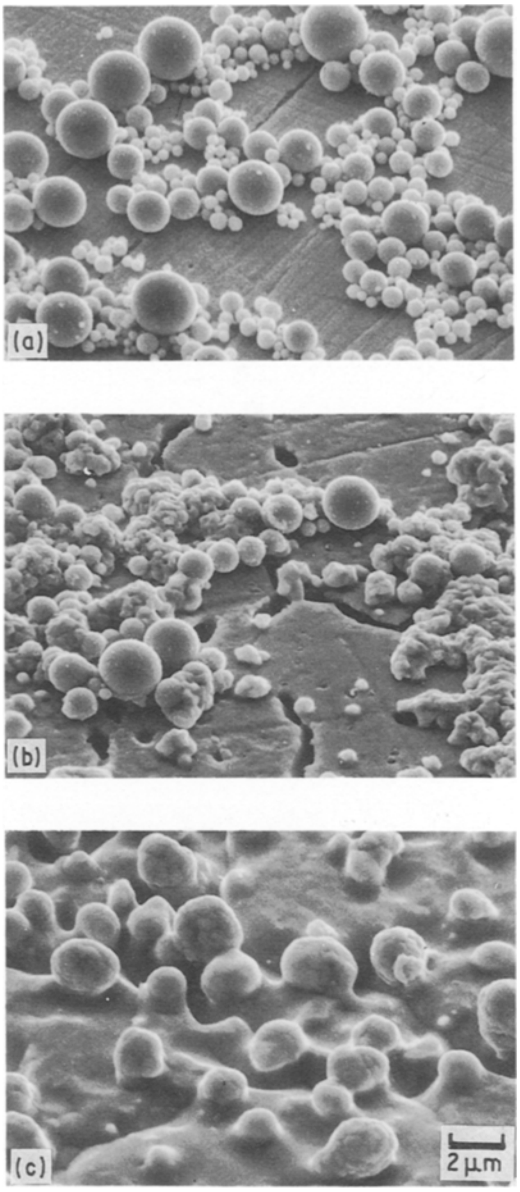

Figure 7 Change of palladium particles dispersed on a silver plate by heating in air for 20 min. (a) Before heating, (b) heated at 300 °C, (c) heated at 400 °C.

3.3. The oxidation of palladium during heating of powders

The oxidation–reduction of palladium is important in the manufacture of multilayer ceramic capacitors because electrode expansion occurs with oxidation and gas evolution occurs during reduction. It is also important in the fabrication of silver–palladium conductor circuits on alumina substrates for hybrid integrated circuits where the presence of palladium oxide interferes with solder wetting. S. S. Cole, Jr [10] investigated the oxidation–reduction of palladium in the presence of silver by thermogravimetry (TG) and obtained some useful findings using chemically precipitated powders. In the present study, the oxidation–reduction of palladium in silver–palladium alloy powders and powder mixtures was investigated by thermogravimetry (Model 8112H, Regakudenki Kogyo, Co., Japan). Silver and palladium powder mixtures were prepared from powders No. 3 and No. 4

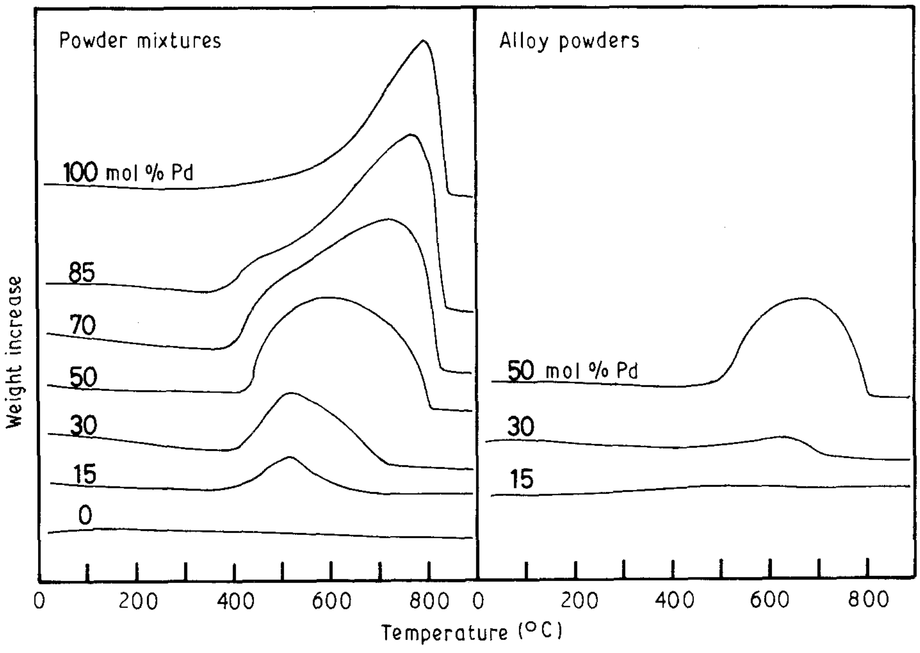

Figure 8 Thermogravimetry (TG) curves of silver–palladium powders heated in air at a rate of 10 °C min^{-1}.

by ultrasonic mixing in acetone. Alloy powder was also dispersed in acetone before use.

Fig. 8 shows the TG curves. The increase in weight corresponds to the amount of palladium oxide formed. A typical finding is the rapid oxidation of palladium at the low temperature of 400–500 °C in the powder mixtures; this is not observed in alloy powders and pure palladium powder. The alloying reaction in the mixture of silver and palladium powders occurred in the same temperature range as described above. This suggests that the oxidation of palladium is accelerated by the alloying reaction. The oxidation peak in the powder mixture shifts to lower temperatures with a decrease in palladium content as reported by S. S. Cole, Jr. [10]. In the case of alloy powders, on the other hand, palladium oxide is formed at higher temperatures than the mixture. In the alloy powder containing 15 mol % Pd, the oxidation is not detected. The degree of palladium oxidation corresponding to the maximum weight increase in heating curve is shown against the powder composition in Fig. 9. In the powder mixtures, the per cent of palladium oxide formed is nearly constant and larger than in pure palladium powder, presumably because of the rapid oxidation during the alloying reaction. In the case of alloy powders, the per cent of palladium oxide formed decreases significantly with the decrease in palladium content, although the difference is small between alloy powder and powder mixture of 50 mol % Pd. In addition to the difference between the two types of powders, it should be noted that the extent of palladium oxidation of the silver–palladium alloy and pure palladium powders prepared by the spray-pyrolysis technique is much lower than powders prepared by chemical precipitation [10, 11]. This is mainly because a metal particle prepared by the spray-pyrolysis technique has a large crystallite size or low specific surface area, and low activity attributed to the fusion during preparation [3]. In chemical precipitation, it is difficult to prepare such particles.

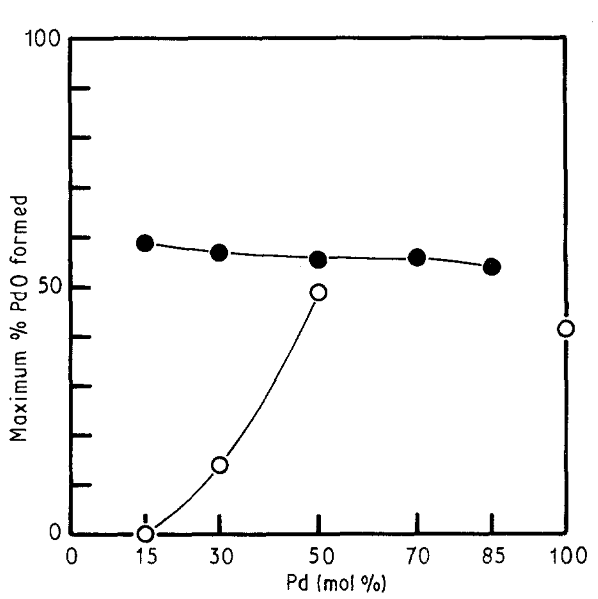

Figure 9 Maximum per cent of palladium oxide formed during heating in air at a rate of 10 °C min^{-1}. (●) powder mixtures, (○) alloy powders.

Palladium oxide formation from silver–palladium alloy may be represented by the equation

$$\mathrm{Ag_mPd_{n+1}} + 1/2\,\mathrm{O_2} = \mathrm{Ag_mPd_n} + \mathrm{PdO},\ \Delta G_1 \qquad (1)$$

The free energy change in this reaction, ΔG_1, is given by the sum of the free energy changes of the following two reactions

$$\mathrm{Ag_mPd_{n+1}} = \mathrm{Ag_mPd_n} + \mathrm{Pd}, \qquad \Delta G_2 \qquad (2)$$

$$\mathrm{Pd} + 1/2\,\mathrm{O_2} = \mathrm{PdO}, \qquad \Delta G_3 \qquad (3)$$

The value of ΔG_2 is given at 1000 K, but the temperature dependence is not given in [12]. However, it may be neglected in the estimation of ΔG_1 because the temperature dependence of ΔG_3 is very large [13]. Fig. 10 shows ΔG_1 in air. At a given temperature, ΔG_1 increases as the palladium content decreases. In other words, the formation of palladium oxide from

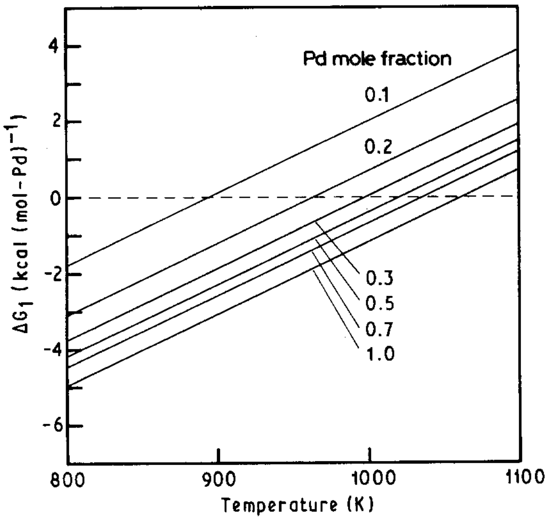

Figure 10 Free energy change in palladium oxide formation from silver–palladium alloy in air.

$$Ag_mPd_{n+1} + 1/2\,O_2 = Ag_mPd_n + PdO,\ \Delta G_1$$

silver–palladium alloy becomes unfavourable thermodynamically with a decrease in the palladium content. This thermodynamic tendency can explain the lowering of the decomposition temperature of palladium oxide in TG measurements as seen in Fig. 8. The same explanation may be applied for the fact that oxidation of the silver–palladium alloy powder containing 15 mol % Pd was not observed.

4. Conclusion

The particular behaviour observed in sintering and palladium oxidation of the silver–palladium alloy powders prepared by the spray-pyrolysis technique is mainly attributed to the compositional uniformity, large crystallite size, and low surface activity. It is difficult to prepare such particles by any other methods. Although an actual application to electronic devices was not carried out in this study, it will surely exhibit excellent capabilities in major cases.

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