Evolution of Particle Structure during the Formation of Single-Crystal Spherical Palladium Particles by Spray Pyrolysis

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The evolution of particle structure in the formation of submicron single-crystal spherical palladium particles by spray pyrolysis was investigated by observing the change of the morphology and internal structure of the particles during heat treatment. Below 700°C oxide particles with solid and homogeneous structure were formed. Decomposition of PdO took place within a particle above 700°C and an oxide layer was left on the surface of palladium particles until the decomposition is completed. The yielded palladium clusters sintered immediately and the particles shrunk uniformly and dramatically as the decomposition reaction took place. The shrinkage of particles was completed almost simultaneously as the decomposition of PdO was completed, however, a little expansion was observed which is attributed to the decomposition of entrapped oxide in the particles. High temperature lead to rapid grain growth within a particle and allowed the formation of single-crystal palladium particles in the spray pyrolysis process. Particles prepared by ultrasonic spray pyrolysis at above 1200°C were single crystals and had clean surface without any amorphous or oxide layer.

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1. Introduction

Oxidation of palladium powder which is accompanied with a volume change of 68% has been considered to result in the delamination between electrodes and ceramic layers during the co-firing process of multilayer ceramic capacitors (MLC). As the oxidation rate of palladium powder decreases with the crystallite size of the powder, spray pyrolysis technique has been applied to prepare palladium and other metal powders in recent years. The particles experienced high temperature in aerosol state so that good crystallinity is expected by this method. Pluym et al. prepared palladium powder at 1000°C but the powder was experienced high temperature in aerosol state so that good crystallinity is expected by this method. Pluym et al. prepared palladium powder at 1000°C but the powder was reported to be oxidized completely when heated in air. This is attributed to the low pyrolysis temperature (1000°C) applied in the preparation. We have reported that oxidation of palladium powder can be reduced to 40–60% of theoretic oxidation by an in situ single-crystallizing process. In this paper, we refer to the process of a particle which undergoes intraparticle sintering and grain growth to form a single-crystal particle as single-crystallizing, to distinguish it from the crystallizing of an amorphous phase. There have been numerous studies on the drying of a droplet but little effort to clarify the formation mechanism of particle structure after a dried particle is formed.

However, knowledge of the process from a solid precursor particle to the final product particle during spray pyrolysis is necessary to understand the nature of the process and to control it. In this paper we report the formation of single-crystal palladium particles by spray pyrolysis method and the evolution of particle structure in the process.

2. Experimental

2.1 Powder preparation

Palladium powders were prepared from 0.5 mol·dm⁻³ Pd(NO₃)₂ (Toyo Chem. Co., Ltd.) solution. The synthesis apparatus was composed of an ultrasonic atomizer, a horizontal reaction tube which was heated by three furnaces for the drying stage (T₁), pyrolysis stage (T₂) and the crystallizing stage (T₃) and a filtering system for collecting the formed particles. Temperatures of the three furnaces were essentially set at T₁=300°C, T₂=600°C and T₃=800–1400°C, respectively. The linear flow rate of carrier gas was 2.6 cm·s⁻¹ and the soaking times of droplets/particles within the three reaction zones were estimated to be about 11s, 19s and 27s, respectively, in all runs.

2.2 Characterization

Morphological features of the particles were observed with a scanning electron microscope (SEM; JEOL, JSM-T200). Size distribution of the particles was measured by directly counting all particles from enlarged SEM photographs of a randomly selected area of more than 200 particles. An X-ray diffractometer (XRD; Philips, PW1700) was used for phase analysis of the prepared powders. Crystalite sizes of the powders were determined by X-ray diffraction line broadening method. Specific surface areas (SSA) of the powders were measured by BET nitrogen adsorption method (Micromeritics, Flowsorb II 2300). To investigate the internal structure of particles, a powder was embedded into an epoxy resin and then sliced to 40–80 nm in thickness by ultramicrotomy (Reichert-Nissei, Ultracut N). Microtome sections were observed with a transmission electron microscope (TEM; JEOL, JEM-200CX) and a high resolution TEM (HREM; Philips, CM 200). Thermal analysis (TG-DTA; Rigaku, TAS–200) was carried out at a heating rate of 10 and 20°C·min⁻¹ in flowing nitrogen or air atmosphere.

2.3 Study method for the formation mechanism of particle structure

To investigate the structural evolution of particles on heating, some oxide particles formed at the second stage
(T1=300°C, T2=600°C) were collected for heat treatment experiments. Some particles were dispersed onto an alumina substrate and heated cyclically in nitrogen at 800°C. After every cycle of heat treatment, the same particles on the marked places on the substrate were observed with a FE-SEM, and XRD was carried out parallelly to monitor the composition change of the powder. Besides, batch heat treatment was carried out by heating the powder of about 2 g in a platinum crucible at 800-1050°C in flowing nitrogen for 5 min to 85h. In both cases the sample was put into a quartz tube that was heated at the determined temperatures and air quenched at various holding time. The times for raising and lowering the temperature of the samples were around 2 min. The resulted particles were sliced by ultramicrotomy to observe the development of particle structure.

3. Results and discussion

3.1 Dependence of particle structure on the formation temperature

Figure 1 shows the TEM photographs of the microtome sections of the particles prepared at various temperatures. Among which the powders prepared below 800°C were collected after the mists were transmitted only through the first two reaction zones. Figure 1(a) shows that the particles formed at T1=T2=200°C were solid spheres with uniform particle structures. Halo rings in the diffraction pattern indicates that the particles were amorphous. The XRD patterns of the powders formed below 700°C had broad peaks of palladium oxide or its hydrate (PdO·xH2O) without any nitrate residues. As a small weight loss was observed around 100°C in the TG curve of the powders, it is reasonable to consider the existing phase as PdO·xH2O. For particles prepared at T1=300°C and T2=600°C, TEM photographs showed that the crystallites was 10-30 nm in size and the diffraction rings became dotty (Fig. 1(b)). TG-DTA analysis showed that the decomposition of PdO began at 670-690°C and was completed at 790-800°C in nitrogen atmosphere. Figure 1(c) shows the structure of the powder prepared at T1=300°C and T2=800°C when PdO was partially decomposed. The surface of the particle was porous and consisted of small grains. However, grains of about 50 nm in size with necks formed between each others were observed at the interior of the particle. The diffraction patterns indicated that these large grains were palladium and the small ones near the particle surface were PdO. It is obvious that the yielded palladium crystallites had sintered immediately subsequent to the decomposition of PdO.

In the range of T3=1000-1200°C, most of the formed particles were polycrystalline palladium. Single-crystal palladium particles shown in Fig. 1(d) were obtained at the typical condition of T1=300°C, T2=600°C and T3=1200°C. Although some complex contrast due to the microtome-caused lattice distortions can be seen in the TEM photographs, the diffraction pattern of the whole particle showed a typical pattern of single-crystal cubic palladium along the [100] direction. Figure 2 is the HRTEM photograph of a particle showing the lattice image of cubic palladium. The interplanar spacing measured from the photograph was 0.22 nm, which agrees favorably with that of [111] of cubic palladium. The lattice image spread to the most surface of the particle. This indicates that no amorphous phase nor oxide layer was formed on the particle surface.

The proportion of single-crystal particles among a powder increased with T3. For the powder prepared above 1200°C, almost all particles were single-crystals. However, it was found that excessively high temperatures caused the evaporation of palladium because palladium has the highest vapor pressure in the platinum family metals and evaporates seriously near and above its melting point (1552°C). Therefore, T3 was set below 1400°C to allow a particle to grow to a single-crystal without evaporation of palladium. The surface of the particles was smooth and no tiny particle was found for all batches prepared at T3 ≤1400°C.

3.2 Development of the particle morphology

To investigate the structural evolution of particles on heating, some oxide particles formed at T1=300°C, T2=600°C and dispersed onto an alumina substrate were heated cyclically in nitrogen at 800°C. Figure 3 shows the mor-
Fig. 2. HRTEM image near the surface of a palladium particle prepared at $T_1=300^\circ\mathrm{C}$, $T_2=600^\circ\mathrm{C}$ and $T_3=1200^\circ\mathrm{C}$.

Fig. 3. SEM photographs showing the morphological change on heating of the oxide particles prepared at $T_1=300^\circ\mathrm{C}$ and $T_2=600^\circ\mathrm{C}$. (a) prior to heating, and after keeping at $800^\circ\mathrm{C}$ for (b) 0 min, (c) 5 min and (d) 60 min.

Fig. 4. Change of particle sizes with the holding time at $800^\circ\mathrm{C}$ in nitrogen.

Fig. 5. Structure development of the particles during heating at $850^\circ\mathrm{C}$ with heating time. As PdO was decomposed, at first a porous structure was formed. Consistent with the observation for the particles prepared at $T_2=800^\circ\mathrm{C}$ (Fig. 1(c)), large palladium crystallites of 50–100 nm in size were observed at the internal region of the particle at the beginning.
of the heat treatment (Fig. 5(b)). As the decomposition temperature of PdO is much higher than the sintering onset of ultrathin palladium particles (about 0.3 times melting point, i.e., below 300°C), the yielded palladium crystallites sintered immediately as they were formed by the decomposition of PdO. The initial sintering rate of the yielded palladium crystallites was very fast and just limited by the decomposition reaction of PdO. Because the palladium crystallites initially formed were separated by PdO, numerous nuclei for grain growth were formed so that a porous particle structure was formed first (see Fig. 1(c) and Fig. 5(b)).

After heated for 1h at 850°C, the oxide content of the powders decreased to less than 1 mass%. The particle was composed of a core of palladium crystals and a thin surface layer of oxide as shown in Fig. 5(c). This surface layer of thin PdO crystallites, though being very thin, existed until heated for 5h at 850°C. A layer of oxide was also observed on the surface of some particles prepared at T3=1000°C. This is attributed to that the decomposition of PdO takes place simultaneously within a particle. As the sintering of palladium crystallites goes on, palladium condenses to the center of particle. A dense core of palladium is thus formed and a layer of PdO is left on the surface of the particle, until the decomposition reaction is completed. Most of the dense polycrystalline particles became single-crystals after heated for 20h at 850°C (Fig. 5(d)).

Figure 6 shows the change of specific surface area and crystallite size of the powder with heating time for the same samples shown in Fig. 5. Specific surface area of the powder increased as the decomposition reaction took place and then decreased near linearly. Decomposition of the oxide gave rise to smaller crystallites and open pores as the gas was released, thus increased the surface area of the powder. However, sintering of the product metal decreased the surface area of the powder. On the other hand, the crystallite size of palladium kept growing as the powder was heated. After heated for more than 5h, the crystallites became larger than the measurable size by XRD line profile method of about 200 nm. It became the same as the particle size after heated for more than 20h that most particles became single-crystal particles.

3.4 Intraparticle reaction and intraparticle sintering during the spray pyrolysis process

The above results showed that the formation process of the particle structure is a complex process composing the intraparticle reaction (decomposition of PdO), the intraparticle sintering and the grain growth of palladium. The combined effects of these processes determine the final structure of palladium particles. The initial crystallites of palladium were estimated to be around 10–20 nm in size calculated from the observed crystallite size of PdO. Metal particles of this size have very fast neck-growth rate and diffusion rate. For this reason, the initial stage of intraparticle sintering of palladium is considered to be completed in a short time. It is observed that the shrinkage of particle was almost completed simultaneously with the decomposition of PdO (Fig. 3). This suggests that the grain growth within a particle takes most of the time in this process. Here the grain size is the crystallite size in a particle which can be measured with BET (d_BET) and X-ray diffraction line broadening method (d_XRD). The data of the latter part of the heat treatment process (Fig. 5 and Fig. 6) were plotted and interpreted according to the normal equation of grain growth

\[ \frac{dp}{dt} = k \]  

where \( d_0 \) and \( d \) are the grain size at the start point and time \( t \), \( p \) is a constant. As shown in Fig. 7, straight lines were obtained by log-log plotting of \( d \) vs. \( t \). The slopes of the curves were not 0.5 but around 0.27, possibly due to the small size of the sintering body which suppresses the growth of the grains within a particle. Smaller \( p \) is considered to be efficient for Eq. (1) when the grains grow to near the saturation grain size. When a grain boundary migrated to the particle surface, it can not move forward any more so that the grain growth rate is decreased.

As the grain growth is limited within one particle, higher temperature decreases the time needed for completed grain growth, i.e., formation of a single-crystal particle. Shimada et al. showed recently that as the sintering within an agglomerate of Ag or TiO\(_2\) goes on, the primary particle size increases and the agglomerate size decreases and finally they become the same. The time needed for this change decreases with temperature. In the present case, this time was observed to be 20h at 850°C but only 1h at 1000°C in the heat treatment experiment. This indicates that high temperature is efficient and necessary for the formation of well crystallized particles in a very short time by spray pyrolysis. In our study, a crystallizing temperature over 1200°C was found to be necessary for single-crystallizing.

4. Conclusions

Evolution of the structure of palladium particles was investigated.

(1) Particles formed below 700°C comprise nanometer-sized palladium oxide crystals. Internal structure of the particles is solid and homogeneous.

(2) Decomposition of PdO takes place simultaneously within the particle above 700°C. The yielded palladium crystallites sinter immediately when they are formed and con-
dense subsequently to the center of particle.

(3) Shrinkage of the particles is uniform and is completed almost simultaneously as the decomposition reaction. Evolution of gas by the decomposition of the oxide entrapped in a palladium particle caused a little expansion of particle which is considered to be the main reason of hollow particles.

(4) Single-crystal particles obtained through complete intraparticle sintering and crystal growth have clean surface without any amorphous phase or oxide layer.

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