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PALLADIUM METAL AND PALLADIUM OXIDE PARTICLE PRODUCTION BY SPRAY PYROLYSIS

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ABSTRACT

Spray pyrolysis was used to produce dense, spherical palladium metal particles at and above 900 °C in air and 800 °C in nitrogen, well below the melting point of palladium (1554 °C). Palladium oxide particles were produced at lower temperatures. At 500 °C the PdO particles were composed of nanocrystalline grains 5 to 15 nm in diameter and had surface areas of 30.2 to 32.8 m²/g. The particles became less porous and less polycrystalline as temperature increased. At 800 °C the PdO particles were polycrystalline with grains of 20 to 50 nm and a surface area of $3.23 \text{ m}^2/\text{g}$. The Pd particles produced at 900 °C by decomposition of the oxide were single-crystalline and fully-dense. These observations are consistent with the formation of porous but not hollow aggregates of PdO at lower temperatures, which can be densified in the gas phase to form solid particles of Pd above 900 °C.

MATERIALS INDEX: palladium, oxides, nanophase

Introduction

A wide variety of industries have applications for palladium metal, such as the dental, medical, chemical, and automotive industries (1). Palladium oxide has semiconductive and catalytic properties, and can also be used as a pH indicator (2,3). The electronics industry is also an important consumer of palladium as it requires palladium particles to form thick conductive films for use in multi-layer capacitors and other electronic components. As the uses for palladium

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become more specialized, metal particles with improved characteristics must be produced which will form a material with the desired properties. In the case of thick-film applications, the ideal particles should be spherical, monodisperse, unagglomerated, micron-sized or smaller, solid, and have a controlled microstructure.

Liquid-phase routes for the production of fine metal particles are well established (4). For example, metal powders such as Pd, Ag, Ni, and Cu are currently produced mainly by precipitation from solution. However, the particles produced by this method are typically agglomerated, non-uniform, impure, and irregularly-shaped.

In this paper we discuss a gas-phase approach, spray pyrolysis, for Pd powder generation. A precursor metal salt solution is atomized by an aerosol generator, the droplets are evaporated and reacted in a furnace, and the metal particles formed by the decomposition reaction are collected on a filter (5,6). The parameters controlling particle properties in spray pyrolysis are reactor temperature, solution concentration, aerosol droplet size, reaction atmosphere, and residence time. The goal of this work was to examine the effects of the variables on the properties of the resulting palladium particles, and to find the operating conditions necessary to produce particles with the above desired characteristics.

A key problem that is often encountered when using spray pyrolysis is the formation of hollow or porous particles (5,6). This problem has been overcome in the case of certain metals by melting the particles in the gas phase. The production of Pd powders by spray pyrolysis has been studied previously (7,8), but solid spherical particles were obtained only above the melting point of palladium (1554 °C). Similarly, other dense metal particles including Cu, Ni, and Ag have been produced by spray pyrolysis above their melting points (9,10,11). However, in a previous study we have shown that dense Ag particles can be produced at 360 °C below the melting point (12). In this work, we demonstrate that solid Pd particles can also be produced well below the melting point of Pd.

A difficulty involved in the production of palladium metal is the formation of the unstable oxide PdO. Palladium oxidizes at low temperatures (≈400 °C) to form PdO, subsequently altering particle morphology and physical properties and having adverse affects on the performance of components consisting of the material. The palladium oxide reduces back to palladium metal at about 800 °C depending on other parameters. Thus, the conditions affecting the palladium oxidation-reduction reaction, and the properties of the palladium oxide particles formed under the varying conditions were also examined.

Experimental (UHP) Nr. or Air Carrier Gas Figure Cauge TSI or Ultrasonic Aerosol Generator Gas Flowmeter

FIG.1

Experimental apparatus for Pd production by spray pyrolysis.

The experimental apparatus used in this study is illustrated in Figure 1 and was discussed in earlier work (12). A carrier gas was directed through an aerosol generator where a palladium nitrate $(Pd(NO_3)_2)$ solution was atomized into aerosol droplets. The droplets were passed through a hot-wall reactor where they evaporated and the metal salt solution decomposed to form the palladium or palladium oxide particles. The particles were then collected on a heated filter. A pressure gauge was placed before the reactor to monitor any obstructions in the system or the filter, which would cause a pressure increase. A thermocouple monitored the temperature of the filter, which was maintained near 60 °C to prevent water condensation. Vol. 28, No. 4

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The first set of experiments used air at 35 psig as a carrier gas, a TSI-3076 constant output atomizer as the aerosol generator, humidifying columns before the reactor to reduce evaporative losses of the water, and a 0.5 M Pd(NO₃)₂ precursor solution. The second set of experiments used ultra-high purity nitrogen (UHP N₂) as the carrier gas, a modified ultrasonic Pollenex home humidifier as the aerosol generator, no humidifying columns, and a 1.9 M Pd(NO₃)₂ precursor solution. The reactor temperatures ranged between 300 and 1000 °C, and the residence times correspondingly ranged between 38 and 13 seconds.

The reactor was a 3-Zone Lindberg furnace with a mullite tube (Coors 152.4 cm, 9 cm outside diameter, 8 cm inside diameter) having a 91 cm heated region. The filter holder (Gelman 147 mm Stainless Steel Filter Holder) supported the filter (Tuffryn 142 mm, HT-45Ø, 0.45 μ m) outside the furnace.

Scanning electron microscopy (SEM) was used to determine particle morphology and approximate size, transmission electron microscopy (TEM) and selected area electron diffraction (ED) were used to determine particle microstructure, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to determine particle purity, and x-ray diffraction (XRD) was used to determine the phases present in the powder. Also, Brunauer, Emmett, and Teller (BET) surface area analysis was used to determine powder surface areas.



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Phase Formation

Palladium metal was the primary phase present when the reactor temperature was 900 °C and above in air, and 800 °C and above in nitrogen. XRD indicated the presence of only traces of PdO remaining at these temperatures (Fig. 2 a,b). The reduction reaction in an N₂ atmosphere was favored over the reaction in air, and therefore the reduction reaction in N₂ went to completion at a temperature 100 °C lower than in air. PdO was the primary phase present in all powders formed at lower temperatures, which ranged from 500 through 700 °C in nitrogen, and 300 through 800 °C in air. Traces of Pd metal appeared in the 800 °C air powder and in the 700 °C nitrogen powder (Fig. 3 a,b).

The extent of the Pd(NO₃)₂ decomposition reaction was determined as a function of reactor temperature by TGA analysis. A 16% weight loss was observed for the sample formed in air at 300 °C indicating that the Pd(NO₃)₂ had not completely reacted to form PdO. The powders produced at temperatures above 300 °C in air did not exhibit TGA weight losses, and thus the decomposition reaction went to completion at roughly 400 °C and above. The decomposition reaction was complete for the powder produced at 500 °C in N₂, which was the lowest temperature run in nitrogen.



(a)



(b)





(d)

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(e)

FIG.4

SEM photographs of PdO and Pd powder formed at (a) 900 °C in air with the TSI, (b) 500 °C in air with the TSI, (c) 900 °C in N₂ with the ultrasonic, (d) 500 °C in N₂ with the ultrasonic, (e) 700 °C in air with the TSI.

Particle Size and Morphology

The sizes of the Pd and PdO particles were estimated from SEM photographs of the powder samples (Fig. 4). All the particles formed in air were produced with the TSI generator and were 1 μ m in diameter or less for all temperatures. The particles produced with the above conditions at higher temperatures (ie. 900 °C) (Fig. 4a) appeared to be smaller than particles produced at lower temperatures (ie. 500 °C) (Fig. 4b). All the particles formed in N₂ were produced with the ultrasonic generator. At 900 °C (Fig. 4c) these particles appeared to be 1 μ m or less in diameter. However, a few particles produced under these conditions at 500 °C (Fig. 4d) ranged between 1 μ m to 5 μ m in diameter. The observations above suggested that densification of porous particles occurred at higher temperatures. The larger particles from the set of experiments run in the N₂ atmosphere with the ultrasonic generator were due to both the higher precursor solution concentration and the larger aerosol droplet size produced by the ultrasonic generator. Palladium particles ranging in size from $0.5 - 0.8 \,\mu\text{m}$ were produced by Nagashima et al. (1987) using low solution concentrations (0.01 - 0.1 M) but particle size was not substantially less than the particles produced with the higher solution concentrations in these experiments. The particle size dependence on concentration and droplet size has been discussed earlier for the Ag/AgNO₃ system (12), where it was determined that particle size had only a weak dependence on solution concentration but a much stronger dependence on droplet size.

The morphologies of the particles were similar for experiments with air and nitrogen. The surface features of the particles were not dependent on solution concentration, droplet size, or reaction atmosphere, but seemed to depend only on temperature. The PdO particles produced at 500 °C were spherical, but exhibited large cracks and fractures at the surface (Fig. 4 b,d). Additionally, these particles were polydisperse and appeared porous. At 700 °C (Fig. 4e) the PdO particles had a layered morphology, with some particle shells present. These particles also had some surface porosity. The surfaces of the Pd particles formed at 900 °C (Fig. 4 a,c) were lumpy, however they did not appear to be porous. Also, at 900 °C all the particles were completely dense and had a narrower size distribution than at lower temperatures where different levels of densification were attained in the particles. No shells were present at 900 °C which was probably due to the higher densification rate of the Pd particles at this high temperature than for the PdO particles (13) at 800 °C and below.

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Microstructure

The microstructure of the particles depended strongly on reactor temperature. Surface areas for PdO powders formed in air and in nitrogen at 500 °C, 30.8 and 32.8 m²/g respectively, were much higher than those calculated for solid particles, indicating that the particles were not dense at this temperature. This was in agreement with SEM surface morphology observations. Particles formed at 600 °C in air had a surface area of only 9.06 m²/g, which indicated that densification in the aerosol-phase had begun at 500 °C. The particles produced in air at 700 °C had a surface area of 4.73 m²/g, consistent with the minimal porosity observed in the SEM photographs. The surface areas for Pd particles formed at 900 °C in air and nitrogen were 2.53 and 1.78 m²/g respectively, indicating that the particles were dense. This result was also in agreement with the SEM determination that dense Pd spherical particles were produced at 900 °C in air. This is a significant result because it has been reported that Pd particles with surface areas near 3.5 m²/g and below exhibited uniform shrinkage during sintering, with no structural defects and low resistivities (14).







FIG.5

TEM photographs and ED patterns of PdO and Pd powder formed at (a) 500 °C in air with the TSI, (b) 800 °C in air with the TSI, (c) 900 °C in air with the TSI, (d) 500 °C in N₂ with the ultrasonic, (e) 900 °C in N₂ with the ultrasonic.

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The dependence of microsctructure on reactor temperature was also examined by TEM. The TEM and electron diffraction results (Fig. 5) explained the dependence of surface areas and porosities of the powders on temperature. The PdO particles produced at 500°C in both air and nitrogen were polycrystalline as shown by their electron diffraction patterns (Fig. 5 a.d). The TEM photographs showed that each particle was composed of agglomerates of small crystallites, yet were not The crystallites were 5 to hollow shells. 15 nm in diameter as calculated from the peak widths of the XRD patterns and from the TEM photographs. The PdO particles formed at 800°C in air were polycrystalline (Fig. 5b) consisting of grains 20 to 50 nm in diameter. The electron diffraction pattern of individual particles again showed polycrystalline particles, but with larger grain sizes than in particles produced at 500°C. The narrowing of the XRD peaks also indicated larger grain sizes (Fig. 3a). The TEM photographs show that there was less porosity in particles formed at 800°C than at 500°C. The particles formed at 900°C in both air and nitrogen were dense, spherical, and singlecrystalline as determined from TEM and electron diffraction (Fig. 5 c,e). The narrow XRD peaks also suggested that the particles were single-crystalline (Fig. 2a). Additionally, the TEM photographs showed dark spheres with no light regions present, suggesting that the particles were completely densified at 900°C. Thus, dense Pd particles were produced far below the melting point (1554°C) which was previously reported to be the necessary temperature for generation of dense Pd particles by this approach (7).

Nanophase PdO formed at 500 °C. Crystalline size: 5 - 10 nm. l'emperature Polycrystalline PdO formed at 800 °C. Grain size: 20 to 50 nm. Reaction and densification. Temperature: 800 - 900 °C. Dense single-crystalline Pd. Temperature: 900 °C. FIG. 6

Microstructure dependence on temperature.

The process of dense Pd particle production is illustrated in Fig. 6. Nanophase PdO is formed at low temperatures (500°C) and grain size increases with increasing raector temperatures. The use of this process to form PdO and other material in nanophase form is reported elsewhere (15). When Pd particles are formed from the reduction of the PdO particles near 900°C, they quickly densify from the polycrystalline state to form single-crystal particles. 376

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Conclusions

Dense phase-pure palladium metal particles were produced by spray pyrolysis at 800 °C and above in N₂, and at 900 °C and above in air. Fully-reacted palladium oxide particles were formed above 300 °C in air and at 500 °C in N₂. The PdO particles produced at 500 °C were spherical, porous, and nanocrystalline. At intermediate temperatures, the particles were polycrystalline, with increasing grain size and decreasing porosity as the reactor temperature increased. Pd particles formed at 900 °C were dense, single-crystalline spheres. Thus, densification was complete at temperatures about 650 °C lower than the melting point of palladium for residence times on the order of 15 seconds.

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