Preparation of Tantalum Nanopowders by Hydrogen Reduction of $TaCl_5$ Vapor

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ABSTRACT

Tantalum powders ranging from 14 to 56 nm in primary-particle size were produced by hydrogen reduction of $TaCl_5$ vapor in a furnace aerosol reactor. The mass of the precursor (solid $TaCl_5$) was instantaneously measured during vaporization by a load cell so that the precursor concentration could be determined and controlled. The phase was amorphous at the reactor temperature of 1000°C, while crystalline at 1400°C. Holding the reactor temperature at 1400°C, the evaporator temperature was varied from 210 to 230°C and the hydrogen flow rate from 0.4 to 2 l/min. The particle size increased with increasing the evaporator temperature due to an increase in $TaCl_5$ vaporization rate, and with increasing the hydrogen flow rate, against the expectation that it would decrease corresponding to the decrease in reactor residence time. The conversion of $TaCl_5$ vapor to tantalum and hydrogen chloride was estimated to be 70% at a reactor temperature of 1400°C. The chlorine and oxygen contents of the powder were measured at 0.3 and 7.0 wt%, respectively.

INTRODUCTION

The high density and ductility of tantalum make it attractive for ballistic applications such as explosively formed penetrators (EFPs). The relatively high cost of tantalum requires consideration of near-net-shape processing from tantalum powders by powder metallurgy. The sinterability of tantalum powders was observed to depend very much on the particle size. For a size of 52 nm, the shrinkage due to sintering commenced at such a low temperature as 800°C, while no shrinkage was seen up to 1700°C with 2 μm powders [1]. In another study of consolidation of tantalum powders, a reduction in sintering temperature by 250°C was observed with a decrease of particle size from < 44 μm to < 100 nm [2]. Nanosized tantalum powders would thus make easier the fabrication of EFPs. The application of these nanosized powders may extend to bio-mechanical micro-devices, high-grade capacitors and so on.

The sodium reduction of K_2TaF_7 is the principal industrial method used worldwide to produce tantalum powders [3]. These powders are, however, of micron size. Nanosized tantalum powders are known to be obtainable by evaporation of a tantalum target by electron beam, laser, or plasma, and immediately cooling the vapor [4], which is called physical vapor condensation (PVC), or by chemical vapor condensation (CVC) in which the tantalum vapor to be condensed is generated by chemical reaction of a precursor vapor. The CVC is usually operable at much lower temperatures compared to the PVC. One example of the CVC is the hydrogen reduction of $TaCl_5$ vapor. This method of tantalum powder production was patented earlier by Brutvan et al. [5]. Then, a pilot-scale production of tantalum nanopowders by the CVC was reported by Winter [1]; very limited data were provided, however. Later Tsukihashi and Iijima [6] reported the effects of reaction temperature, hydrogen partial pressure and evaporation temperature of $TaCl_5$ on the distribution of particle size, morphology and reaction degree. In their experiments, the evaporation rate of the precursor, which is required to determine the precursor concentration in the gas entering the reaction zone, was not available. This is probably due to an inherent difficulty in measuring instantaneous mass of the precursor in vaporization. No data on the crystalline structures were provided, either. Only few reports on the production of tantalum powders by hydrogen reduction of $TaCl_5$ have thus appeared.

In the present work, the mass of the precursor is instantaneously measured during vaporization by a load cell so that the precursor concentration can be determined and controlled, and the crystalline structures of produced particles were investigated with varying reactor temperatures. The effects of the reactor temperature and the evaporation rate on the particle size and size distribution are discussed, and the oxygen and chlorine contents of the powders were determined.

II. EXPERIMENTAL

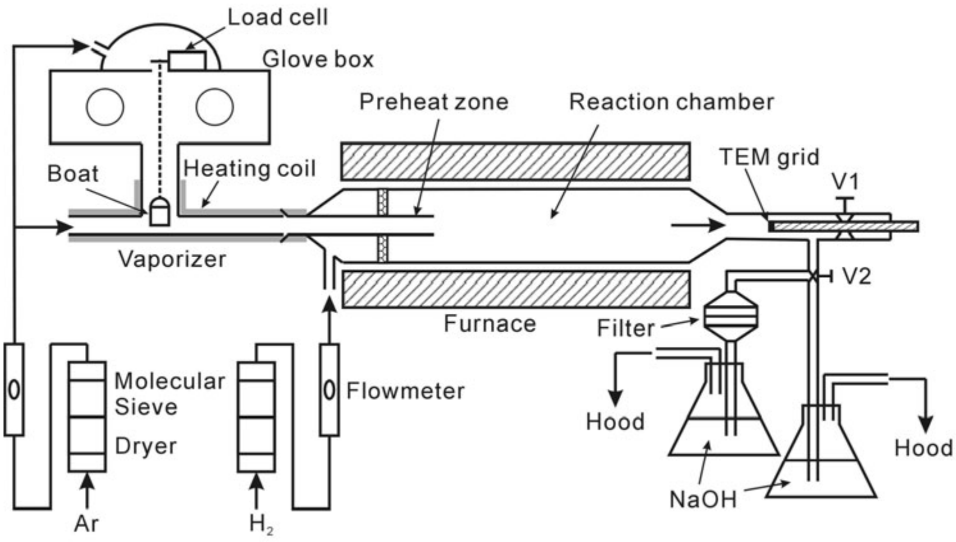


Fig. 1. Experimental apparatus for producing Ta nanopowders.

Figure 1 shows the experimental setup consisting of a deoxidizer, a drying column, a precursor evaporator, a tubular reactor, and a particle collector. The precursor evaporator is made of Pyrex, 2 cm in inner diameter and 30 cm in length, heated by a heating coil, equipped with a thermocouple to measure the precursor temperature, and connected to a reaction tube. A glove box measuring 55 cm by 34 cm by 24 cm is installed overhead for loading the solid precursor, $TaCl_5$ (Aldrich, > 99.99%), to a boat in a moisture-free environment; the precursor is very sensitive to moisture. About 0.3 g of the precursor was used for a run. The boat is suspended by a thin rod hooked up through a flexible bellows to a load cell (Minebea Co., Type UL-20GR). The precursor vaporization begins as soon as the precursor-laden boat is lowered to the evaporator which has already been heated to a desired temperature. During vaporization, the mass of the boat with precursor is measured instantaneously by the load cell.

The reaction tube is made of alumina, 2.7 cm in inner diameter and 54 cm in length, and heated by an electric furnace (Lenton Co., Tube Furnace). The reactor set-temperature was varied from 1000 to 1400°C. Before a run, the evaporator and the reaction tube was purged with argon (99.99%). Hydrogen (99.99%) was then passed through the reaction system. The hydrogen acted as carrier and reducing agent. The hydrogen flow rate was varied to control precursor residence time in the reactor. Produced particles were collected at the exit of the reactor with a Teflon membrane filter (Cole-Parmer, Model Zix 90C), the pore size of which is 200 nm. The gas free of particles was then bubbled through a NaOH solution for removal of the HCl formed by the hydrogen reduction, before being exhausted to the atmosphere.

For the measurement of particle shape, size, and size distribution, a TEM (Carl Zeiss, Model EM912 Omega) was used. From an image obtained by scanning the TEM micrograph, about 300 primary particles were selected and their sizes were determined to calculate the number average diameter using a computer program by which the number of pixels occupied by a particle is counted and converted into a diameter. The X-ray diffraction pattern was obtained by an X-ray diffractormeter (Rigaku, Model RTP 300 RC). The amount of the by-product HCl which had been absorbed in the NaOH solution was determined by chlorine analysis of the solution with an ion-selective electrode (Cole-Parmer, 27502-13).

RESULTS AND DISCUSSION

Precursor vaporization rate

Holding the evaporator temperature at 230°C and the hydrogen flow rate at 2 l/min (STP), the mass of the $TaCl_5$ in the boat, initially at 0.33 g, was measured with time by the load cell. Over a mass change of approximately 90%, the vaporization rate was almost constant at 0.0031 g/s, estimated from the slope of the line fitting the mass change. The amount of residue after the evaporation was negligible. From the vaporization rate and the hydrogen flow rate, the concentration of $TaCl_5$ in the gas admitted to the reactor at 1 atm and 1000°C was calculated at 5.5×10^{-5} mol/l. The concentration could not be determined with the experimental apparatus used earlier by Tsukihashi and Iijima [6].

At the same hydrogen flow rate, the evaporator temperature was reduced from 230 to 210°C by 10°C. The vaporization rate decreased resultantly from 0.0031 g/s at 230°C to 0.0017 g/s at 220°C, and to 0.0014 g/s at 210°C. At the same evaporator temperature of 230°C, the vaporization rate decreased to 0.002 and 0.0016 g/s, as the flow rate decreased to

0.7 and 0.4 ml/min, respectively. This may be due to an influence of the gas velocity on the thickness of the boundary layer across which vaporized precursor must diffuse toward the hydrogen bulk stream. To study the effect of reactor residence time, it is desirable that the other variables including the vaporization rate be kept constant. With the present apparatus, however, a change in hydrogen flow rate affected the vaporization rate as well as the residence time.

Crystalline structures

The x-ray diffraction patterns of produced tantalum powders were investigated with the reactor temperature varied from 1000 to 1400°C holding the evaporator temperature at 230°C and the hydrogen flow rate at 2 l/min. At the reactor temperature of 1000°C, the phase was amorphous. As shown in Fig. 2, peaks indicating the evolution of crystalline structures appeared at 1200°C, and those peaks became sharper as the temperature increased to 1400°C. Compared with the peaks of tantalum provided in JCPDS no. 04-0788 [7], observed peaks shifted towards the lower scattering angles. This is probably due to a formation of hydrides by hydrogen dissolution in the tantalum matrix. It is known that a tantalum absorbs hydrogen, at temperatures higher than 450°C, to the extent of 0.74 hydrogen atoms per tantalum atom [3]. The expansion of the inter-atomic distance by hydrogen dissolution may explain the shift.

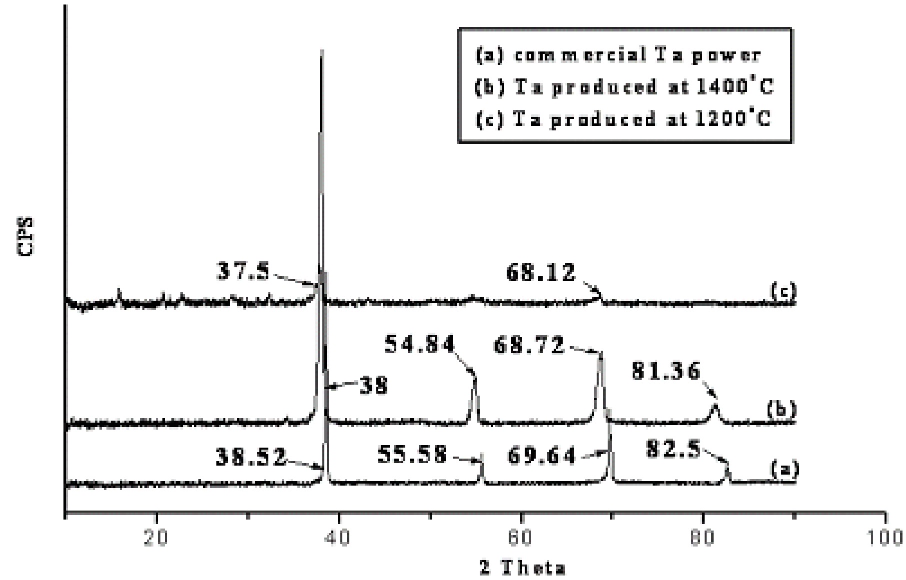


Fig. 2. XRD patterns of as-prepared Ta nanopowders.

Particle morphology and size

The reactor temperature was fixed at 1400°C because the crystallinity was poor at lower temperatures. The evaporator temperature and the hydrogen flow rate were then varied from 210 to 230°C and from 0.4 to 2 l/min, respectively, to study the effects of these variables on particle morphology and size. Produced powders were all in the form of aggregates composed of nanosized primary particles with necking between them. A representative TEM image of the powder, which was produced at the evaporator temperature of 220°C with the hydrogen rate at 2 ml/min., is shown in Fig. 3. By eye inspection, the primary particles are rather uniform in size. Their average primary-particle size was determined at 21 nm, using the method described in the experimental section. The variations with reactor temperature of the primary-particle size and the geometric standard deviation are shown in Fig. 4. As the evaporator temperature increased, the primary particle size increased probably due to an increase in the concentration of $TaCl_5$ vapor entering the reactor. The geometric standard deviation was around 1.25, exhibiting little difference between 210 and 230°C, as determined from the log-probability plot. At the same reactor temperature of 1400°C, Tsukihashi and Iijima [7] reported a particle size of about 40 nm at a vaporization zone temperature of 250°C, smaller than 56 nm that was obtained presently at the evaporator temperature lower by 20°C. The analysis of the particle size difference could not be made because the vaporization rate or the $TaCl_5$ vapor concentration was not available from their work.

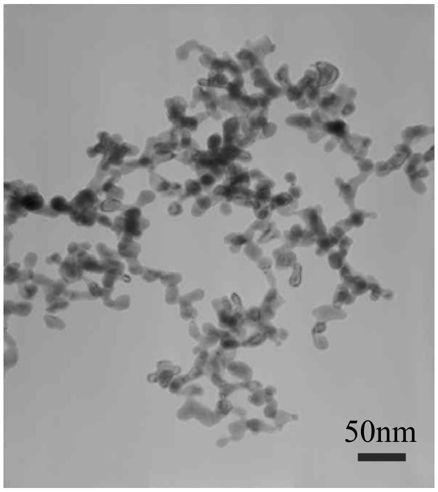


Fig. 3. TEM image of tantalum powders.
(evaporator temp.: 220°C;
reactor temp.: 1400°C; H_2 flow rate: 2l/min)

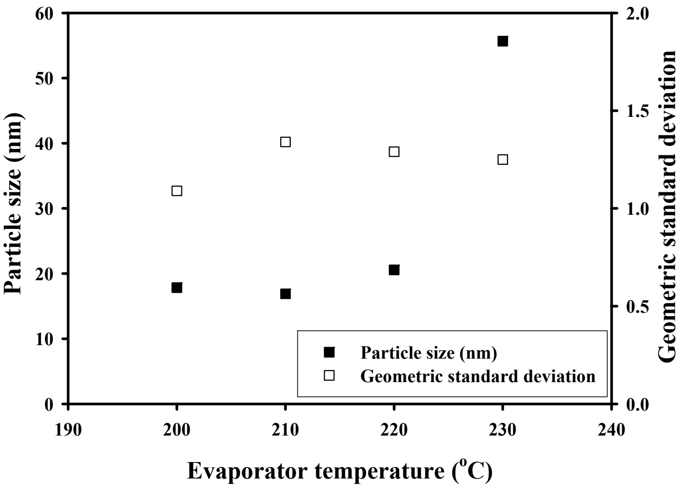
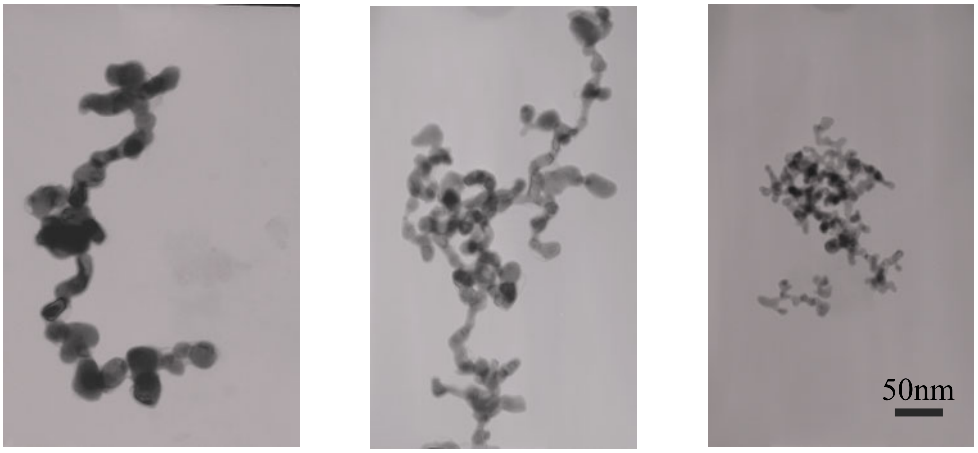


Fig. 4. Effects of evaporator temperature on primary particle size and distribution.

Figure 5 shows the effect of the hydrogen flow rate on particle morphology with the evaporator temperature constant at 230°C. The primary particle size increased with an increase in hydrogen flow rate: 14 nm at the flow rate of 0.4 l/min, 16 nm at 0.7 l/min, and 56 nm at 2 l/min. In this type of reactor, particles are born by homogeneous nucleation and grow by coagulation, surface reaction, and sintering between neighboring particles. An increase in the gas rate must decrease the residence time in the reactor and consequently reduce the chance for particles to grow, leading to a decrease in primary particle size. The particle size, however, increased. This is probably because the increase of $TaCl_5$ vaporization rate accompanied by the increase in hydrogen flow rate, as mentioned earlier, dominated over the decrease in residence time, yielding the overall increase of particle size.



(a) (b) (c)

Fig. 5. Effects of the hydrogen flow rate on particle morphology: H_2 flow rate was (a) 2.1 l/min, (b) 0.7 l/min, and (c) 0.4 l/min.

One particle was chosen out of those produced at the same operating condition as in Fig. 3, and examined by a high resolution TEM. An external layer, 3 nm in thickness, can be seen (Fig. 6). The composition of the layer could not be explicitly determined. It is presumed to be an oxide layer by X-ray photoelectron spectroscopy analysis, as shown in Fig. 7.

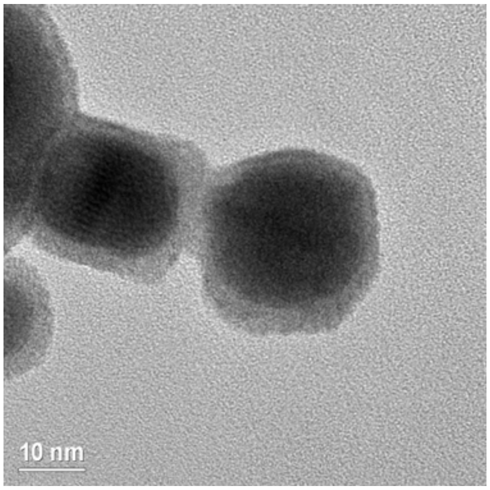


Fig. 6. High resolution TEM image of Ta particles.

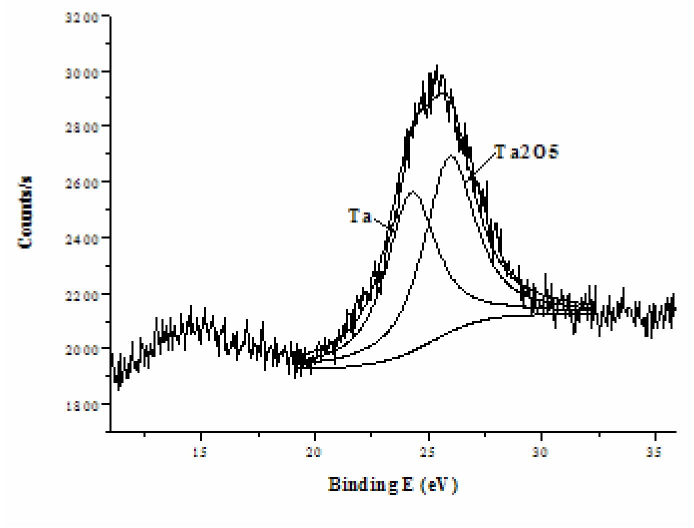


Fig. 7. XPS spectrum of tantalum powders.

Conversion and impurity contents

At the reactor temperature of 1400°C, the evaporator temperature of 230°C and the hydrogen flow rate of 2 l/min, the amount of $TaCl_5$ vaporized and transported to the reactor was measured at 0.72 g or 0.002 mol and that of the HCl absorbed in the NaOH solution was determined at 0.007 mol from the volume of the solution and the HCl concentration measured by the electrode. By stoichiometry that 5 mol of HCl is produced from one mole of $TaCl_5$, the amount of HCl absorbed in the NaOH solution is equivalent to a conversion of 0.0014 mol of $TaCl_5$ to tantalum and HCl. From the amounts of the $TaCl_5$ admitted to the reactor and converted therein, the conversion was calculated at 70%. This is comparable to about 75% reported by Tsukihashi and Iijima [6] at a similar operating condition. Considering that some of the HCl produced may have adsorbed on the powders in the filter and passed the NaOH solution undissolved, actual conversion may be higher than that estimated. The conversion needs to be determined more accurately in the future.

The powder produced at the same operating condition as used for the determination of conversion contained 7.0 wt% oxygen and 0.3 wt% chlorine. It is known that the ductility of tantalum is reduced by increasing the oxygen content [8]. A decrease in particle size should increase the surface area available for oxidation, thereby increasing the oxygen content and resultantly decreasing the ductility.

IV. CONCLUSIONS

Tantalum powders were produced by hydrogen reduction of $TaCl_5$ vapor in a furnace aerosol reactor, the phases being amorphous at the reactor temperature of 1000°C and crystalline at 1400°C. The vaporization rate of the precursor could be determined by measuring the precursor mass instantaneously, which is a contribution of this work. The primary particle size ranged from 14 to 56 nm with the evaporator temperature varied from 210 to 230°C and the hydrogen rate from 0.4 to 2 l/min, holding the reactor temperature at 1400°C. The particle size increased with increasing the evaporator temperature due to an increase in $TaCl_5$ vaporization rate. The particle size was expected to decrease with increasing the hydrogen flow rate, corresponding to the decrease in reactor residence time, but actually increased. An increase in the hydrogen flow rate affected not only the residence time but also $TaCl_5$ vaporization rate, resulting in an overall increase in particle size. The conversion of $TaCl_5$ vapor to tantalum and hydrogen chloride was 70 % at the reactor temperature of 1400°C. The chlorine and oxygen contents in a sample powder were 0.3 and 7.0 wt%, respectively. Further study must follow on consolidation of the nanopowders for practical applications, for which a scale-up for higher production rate is required.

ACKNOWLEDGMENTS

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