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PRODUCTION OF HIGH-PURITY TANTALUM METAL POWDER FOR CAPACITORS
USING SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

In this study, high-purity tantalum metal powder was manufactured via self-propagating high-temperature synthesis. During the process, Ta_2O_5 and Mg were used as the raw material powder and the reducing agent, respectively, and given that combustion rate and reaction temperature are important factors that influence the success of this process, these factors were controlled by adding an excessive mass of the reducing agent (Mg) i.e., above the chemical equivalent, rather than by using a separate diluent. It was confirmed that Ta metal powder manufactured after the process was ultimately manufactured 99.98% high purity Ta metal powder with 0.5 μm particle size. Thus, it was observed that adding the reducing reagent in excess favored the manufacture of high-purity Ta powder that can be applied in capacitors.

Keywords: Tantalum, Self-propagating high-temperature synthesis, Tantalum Oxide, Magnesium, Capacitor

1. Introduction

Tantalum nano- and submicron-sized powders are widely used in capacitors owing to their high dielectric properties as cathode material [1], high capacitance per unit volume, and thermal stability [2], compared with other metal powders. Among the different methods by which such tantalum powders are produced, the method that involves the use of Ta_2O_5 powders can be generally be realized via: 1) the reduction of Ta_2O_5 using elements, such as Mg, Al, Ca, and C [1-3], 2) the electrochemical reduction of Ta_2O_5 [4], 3) the reduction of Ta_2O_5 using a flux, such as CaO and $CaCl_2$, and 4) the use of the vapor of a metal as a reducing agent [5-7]. It is known that the method of reducing Ta_2O_5 to a reducing agent metal has difficulty in controlling the particle size and shape of the powder due to its rapid reactivity [8]. In contrast, the self-propagating high-temperature synthesis (SHS) technique, which in academia and industry, is considered to be environmentally-friendly given that it can be employed to produce relatively high-grade ceramic compounds by utilizing the pyro metallurgical technique, and it does not require a heat source after ignition [9-12], offers advantages such as particle size and shape control via the ignition method and combustion

temperature control. Further, this technique is widely used in the manufacture of nano- and submicron-sized powders [3]. Therefore, in this study, this SHS technique was used to produce Ta powder from Ta_2O_5. Moreover, existing studies on the application of this technique have reported that the control of particle size and shape during this process can be realized via: 1) particle control using a diluent [2,8,13], 2) controlling the density of the initial system [9], or 3) controlling the reaction pressure [8]. However, in this study, we investigated whether particle size control could be realized without using a diluent by adding an excessive mass of the reducing material, which played the role of a diluent. Thus, particle control based on the regulation of the mass of the reducing agent available was successfully realized in this study. Further, this synthesis method also allowed the easy removal of chemical by-products and prevented the formation of secondary phases owing to additional reactions.

2. Experimental

The SHS equipment used in this experiment was fabricated to have a volume of up to 30 L. This SHS equipment and the au-

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tomatic gas discharge device were designed to withstand a maximum internal pressure of 150 bar, and a C-type thermocouple and a digital pressure gauge were installed within the equipment to collect combustion reaction temperature and internal pressure data. Further, to conduct the experiment, Ta_2O_5 powder (purity >99.9%; Daejung Chemicals & Metals Co., Ltd., Korea) was used as the raw material and magnesium (purity >98.5%; Daejung Chemicals & Metals Co., Ltd., Korea) was used as the reducing agent. The aforementioned substances were weighed at a given molar ratio and dry-mixed for 30 min in a glove box purged with argon, which is an inert gas. Thereafter, the mixed powder was loaded into a cylindrical reaction vessel (Φ45 mm and H = 90 mm) and then into the reactor. After the combustion reaction, to remove reaction by-products, a leaching process was performed for 2 h using a solution of HCl (20.63 M), and after washing and drying in a vacuum atmosphere, tantalum powder was obtained. Furthermore, to determine the composition of the prepared tantalum powder, energy dispersive spectroscopy (EDS) was performed, and to determine its structural characteristics, oxygen/nitrogen analysis, field emission scanning electron microscopy (FE-SEM), X-ray diffractometry (XRD), and micro particle size analysis (PSA) were performed.

3. Results and discussion

In this study, to manufacture tantalum powder, Mg was selected among Ca and Mg, which are commonly used as reducing agents for metal oxides, because Mg favors the removal of the reaction by-products resulting from combustion synthesis via HCl as previously described [1] to a greater extent. Thus, the reaction between Ta_2O_5 and Mg, which occurred during the SHS process could be represented by Equation (1).

$$Ta_2O_5 + 5Mg \rightarrow 2Ta + 5MgO \qquad (1)$$
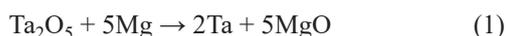
The standard free energy value for Equation (1) was negative and ranged between –224 and –150 Kcal for temperatures in the range 0-2,000°C. Further, the ignition temperature (T_{ig}) for this reaction was 1,076 K, which is a significantly lower ignition point that allows for a stable SHS reaction. These calculations were performed using HSC chemistry 8.0 [14]. Furthermore, combustion rate and reaction temperature are important factors that influence particle growth during the reaction between Ta_2O_5 and Mg, and in a typical self-propagating combustion process,

a separate diluent is added to control them [2,8,13]. However, in this study, rather than separately adding a diluent, Mg, which served as the reducing agent, was added such that its mass was above the chemical equivalent. This enabled the identification of the decrease in reaction temperature, caused by the endothermic reaction of Mg, based on the evaporation of the excessive Mg during the reaction.

As shown in Table 1, the measured reaction temperature ranged from 1,729.8°C (minimum) to 1,927.3°C (maximum). These results suggest that the Mg that did not participate in this reaction acted as a diluent, thereby contributing to lowering the temperature of the entire system. Further, throughout the entire process, the measured combustion speed was approximately 12 mm/s, which basically remained unchanged within a small error range. The decrease in the temperature of the system could be attributed to the addition of an excessive mass of Mg, suggesting that the excess Mg had an insignificant effect on the reaction itself. Further, an overall decrease in the weight of the system was observed after the combustion synthesis. The reaction temperature during the SHS synthesis was greater than 1,089°C, which is the evaporation point of the excess Mg that was added. This observation could be attributed to the loss of Mg owing to the rise in temperature above the boiling point of Mg during the entire process. Thus, the purity of the tantalum powder manufactured through the combustion synthesis process improved. Additionally, there was a slight increase in density during the entire process. This increase in density could be attributed to the partial filling of the pores that were present before the combustion synthesis by liquefied Mg. This is consistent with the results of a previous study, in which Ti metal was manufactured from TiO_2 + Mg through self-propagating combustion [15].

To select a leaching solution for the removal of the reaction by-products that were generated from the combustion synthesis process, thermodynamic calculations were performed using HSC chemistry 8.0 [14]. For better clarity, the reaction equation have been indicated to include the condition of adding 7 mol of Mg, which was associated with the formation a lot of reaction by-products, compared with the other experimental conditions. Equation (2) represents the reaction between Mg and H_2SO_4, which resulted in the formation of H_2O and $MgSO_4$, as well as sulfurous acid gas (SO_2), which is toxic. Thus, H_2SO_4 was not utilized owing to such commercial disadvantages. Further, according to Equation (3), which represents the reaction between Mg and HNO_3, the reaction products were H_2O and $Mg(NO_3)_2$,

TABLE 1

Process results based on reducing agent input

Mg input (mol)	Adiabatic temperature (°C)	Maximum reaction temperature (°C)	Combustion rate (mm/sec)	Weight before/after process (g)	Density before/after process (g/cm³)
5	2826.9	1,927.3	12.86	168.62 /165.33	1.51/1.85
5.5	2772.8	1,783.9	12.74	170.00/168.00	1.55/1.79
6	2659	1,729.8	12.67	174.44/159.20	1.57/1.69
6.5	2551.5	1,769.8	12.43	178.65/167.70	1.54/1.61
7	2449.7	1,759.7	12.21	183.40/162.48	1.45/1.59

alongside nitrous oxide (N_2O), which is a hallucinogenic substance. Therefore, HNO_3 was inappropriate for use as a leaching solution. Furthermore, Equation (4) represents the reaction between Mg and HCl, which resulted in the formation of H_2 gas and $MgCl_2$ only; thus, no toxic gases or hallucinogenic substances were generated, as was the case with the aforementioned reactions involving H_2SO_4 or HNO_3. Thus, HCl was used as the leaching solution. Specifically, to remove residual impurities inside the piezoelectric element, the leaching process was performed using HCl (20.63 M) solution.

$$2Ta + 2Mg + 5MgO + 9H_2SO_4 \rightarrow 2Ta + 7MgSO_4 +$$
$$+ 9H_2O + 2SO_2(g)\ \Delta G^O\ (25°C) = -408.958\ kJ/mol \quad (2)$$

$$2Ta + 2Mg + 5MgO + 15HNO_3 \rightarrow 2Ta +$$
$$+ 7Mg(NO_3)_2 + 7.5H_2O + 0.5N_2O(g)\ \Delta G^O\ (25°C) =$$
$$= -428.594\ kJ/mol \quad (3)$$

$$2Ta + 2Mg + 5MgO + 14HCl \rightarrow 2Ta + 7MgCl_2 +$$
$$+ 5H_2O + 2H_2(g)\ \Delta G^O\ (25°C) = -172.485\ kJ/mol \quad (4)$$
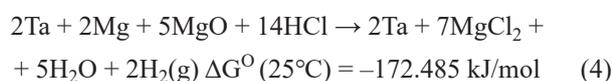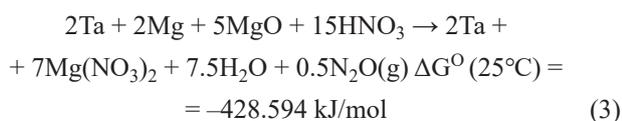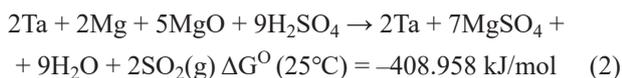
Figure 1 shows the results of the XRD analysis of the tantalum powder manufactured in this study before and after the leaching process. From this figure, it is evident that MgO and $Mg_4Ta_2O_9$ were produced as reaction by-products. Based on existing literature, $Mg_4Ta_2O_9$ is a stable phase reaction by-product generated owing to the reaction between the formed MgO and unreacted Ta_2O_5 [16]. Additionally, unlike the input conditions associated with other reducing agent mass, the generation of the metastable phase, β-Ta, was identified when 7 mol of Mg was added. As shown in Table 1, among the process conditions, which was the low reaction temperature and slow burning rate resulted in the generation of the metastable phase, β-Ta, when the mass of the reducing agent was 7 mol. Further, MgO, one of the reaction by-products, was completely removed via the leaching process (Fig. 1). However, given that it was difficult to remove $Mg_4Ta_2O_9$ via the leaching process, residual $Mg_4Ta_2O_9$

was detected when the mass of the reducing agent was not 7 mol. Therefore, the addition of an excessive mass of Mg played a role not only in controlling particle shape and size, but also prevented the formation of an intermediate phase. Thus, the excess Mg influenced the purity of the particles.

Figure 2, which shows the granular microstructure of the tantalum powders manufactured under different mass of the reducing agent after leaching, indicated that the particles of the manufactured tantalum powder became denser and smaller in size as the mol fraction of Mg increased. Further, the results of the EDS analysis of the fabricated Ta powder showed the presence of residual Mg when the mass of reducing agent, Mg, was in the range 5-6 mol. However, no residual Mg was detected in the Ta powder obtained when the Mg content was 6.5 or 7 mol. These findings indicate that a higher purity of tantalum powder can be expected by increasing the mass of the reducing agent. The results of the FE-SEM analysis of the obtained Ta powders after leaching showed that the overall synthesized primary particles had a network structure. Of these particles, the size of the primary particle obtained when the mass of Mg added was 7 mol, was approximately 1 μm, suggesting that small particles were sintered to secure high porosity, with the smallest possible size of the honeycomb network structure obtained. There are several reports that such structures with high specific surface area, which are advantageous for use as powder material in capacitors, enhance capacitance [17-18]. In Fig. 2, the average particle size for each experimental condition was (a) 1.953 μm, (b) 1.085 μm, (c) 1.082 μm, (d) 0.620 μm and (e) 0.510 μm. As the Mg content increased, the formation of the network of Ta nanoparticles was observed. This can be attributed to the reaction between Mg and Ta_2O_5. As the reaction temperature is increased rapidly, Mg, with a relatively low melting point, envelops Ta_2O_5 in a liquid state followed by vaporization. This causes the Ta particles to sinter and form a network. However, if more than the chemical equivalent of Mg was added, the Mg remaining without vaporization remained inside the product, inhibiting particle growth. It can be assumed that the network
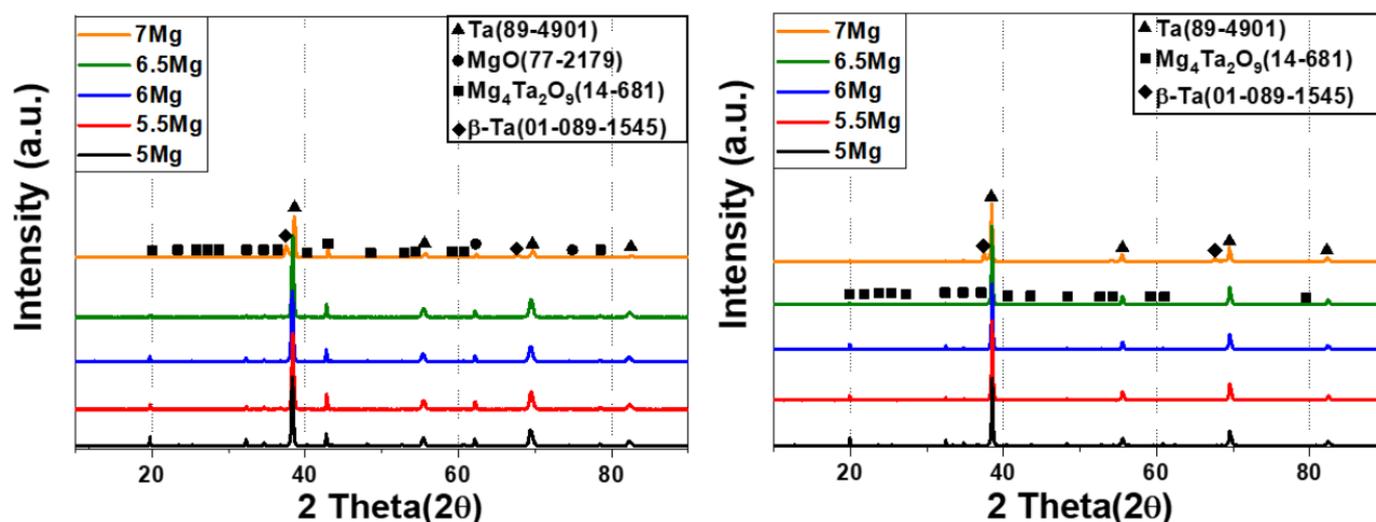
Fig. 1. Results of X-ray diffraction analysis of tantalum powder manufactured under different conditions. (a) Before leaching and (b) After leaching
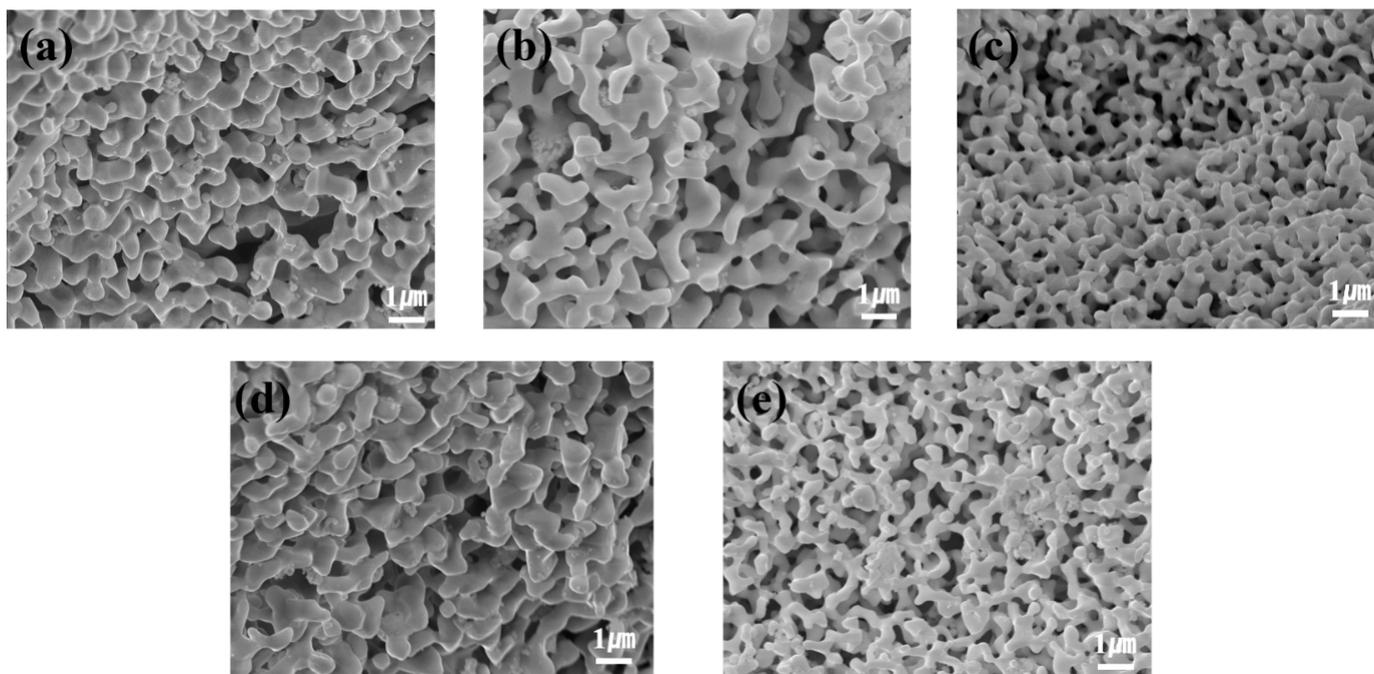
Fig. 2. Results of FE-SEM and EDS analyses of tantalum powder samples under conditions, (a) 5 mol Mg, (b) 5.5 mol Mg, (c) 6 mol Mg, (d) 6.5 mol Mg, (e) 7 mol Mg (magnification = ×10,000)

of Ta nanoparticles was formed based on the theory [19-21] related to nanoparticles [3,8]. Additionally, porous Ta powder nanoparticles with a large specific surface area were generated via adsorption on the surface of Ta particles, which represent the product, followed by cooling and the formation of pores [8].

Figure 3, which shows the data collected based on the use of the wet module of the PSA to measure the particle size and particle size distribution of the manufactured tantalum powder, confirmed the occurrence of larger particles, on average, as the mass of the reducing agent increased. The results also indicated the distribution of Ta particles of various sizes under the condi-

tions of 5-6.5 mol of Mg, while monomodal powder particles were observed when the mass of the reducing agent added was 7 mol, indicating an insignificant difference between the average particle size and D_{50} under this condition. Further, Fig. 3 shows the results of the oxygen analysis of the manufactured tantalum powder using an N/O analyzer. The results obtained indicated that the oxygen content of the Ta powder increased as the number of mol of the reducing agent decreased. This is because in this experiment, the removal of $Mg_4Ta_2O_9$ produced owing to the chemical reaction between the unreacted raw material, Ta_2O_5, and the by-product, MgO, was difficult using HCl as the leaching solution. Moreover, the ICP-OES analysis performed
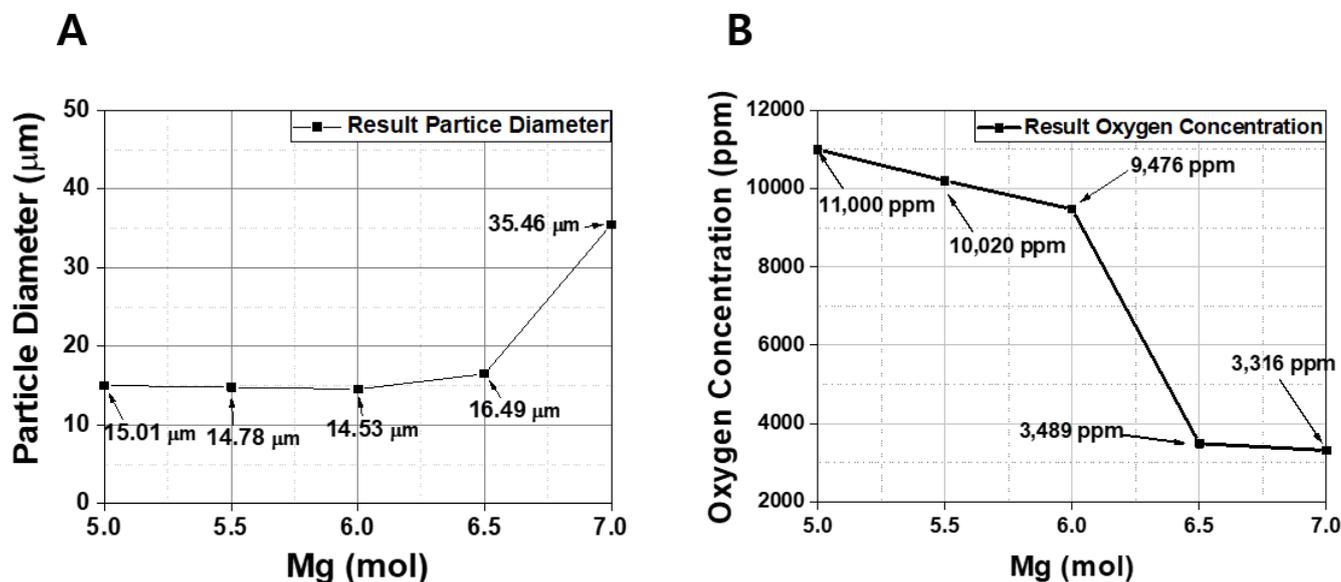
Fig. 3. Acid-purified samples under different conditions. A, Micro Particle Size Analyzer; B, Oxygen analysis results data

to measure the purity of tantalum powder showed that when 7 mol of reducing agent was added, the impurity content was Mg: ND, Ca: 44.5, Cr: 2.282, Mn: 55.13, Ti: 7.172, Zn: 18.76, Zr: 0.461 ppm was detected. In other words, it was confirmed that 99.98% of high purity tantalum was produced. Therefore, based on the basic analysis of the Ta powder manufactured under different conditions (i.e., based on the particle size and shape of the tantalum molecules, as well as EDS, XRD, oxygen content, and ICP-OES analysis results), the optimal mass of the reducing agent was determined to be 7 mol.

4. Conclusions

In this study, the change in the particle properties of tantalum powder with respect to the variation of the input mass of Mg instead of a separate diluent during the preparation of tantalum metal powder for capacitors using the SHS process, was investigated. The following conclusions were drawn.

1. It is possible to control reaction temperature and combustion rate using an excessive mass of Mg, in the absence of a separate diluent. Additionally, the resulting reaction product was adsorbed and cooled on the surface of Ta particles and removed during pickling, resulting in high-purity tantalum powder (99.98%) with average particle size in the order of 0.5 μm that can be used in capacitors.

2. Further studies are needed to develop strategies by which we can suppress and remove $Mg_4Ta_2O_9$, which was produced as a result of the reaction between MgO, a reaction by-product, and unreacted Ta_2O_5 (raw material).

3. Further studies are also needed to control the oxygen content in the produced tantalum powder.

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