

Formation of monodispersed Ta₂O₅ powders

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The Ta₂O₅ powders synthesized by the hydrolysis of tantalum pentaethoxide, Ta(OC₂H₅)₅ in alcoholic solution were monodispersed fine oxide particles, which were a uniform, spherical shape, non-agglomerate, and had a narrow size distribution. They grew to 1.2 μm after ageing for 1 h after hydrolysis. Powder X-ray diffraction and differential thermal analysis–thermogravimetric analysis showed the particles were amorphous and hydrated. These particles lost the water at 290° C and gave well-crystalline Ta₂O₅ at 740° C. Throughout these thermal processes, the particle morphology was kept almost the same.

1. Introduction

Sintering theory in ceramic engineering has been developed; in particular the role of particle rearrangement in the initial sintering stage and the mechanisms of the exaggerated grain growth in the intermediate and final sintering states are becoming clear [1]. These large studies gave the conditions that the starting powders should fulfil in order to produce ceramics with theoretical density at lower temperatures and in a shorter time. The MIT group [2] had proposed a paradigm on the above starting powder, that is, a submicron size, a narrow size distribution, of an equiaxed shape and a non-agglomerated state and high purity. If a starting powder has such characteristics, the powder compact would have the maximum packing density and no driving force on exaggerated grain growth.

In the field of colloid science, monodispersed particles, which are defined such that all particles have the same shape, size and composition, have been studied

and many monodispersed (hydrous) oxide particles have been synthesized mainly by Matijević *et al.* [3, 4] from the standpoint of basic colloid chemistry and corrosion science, but none of the advanced ceramics. Only two cases, such as synthetic precious opal and dental material, have been applied to industrial use [5].

Recently several ceramists have tried to produce monodispersed ceramic particles from the alkoxide process and to use them as the starting powders for advanced ceramics [6–11].

This paper describes the synthesis and thermal change of monodispersed Ta₂O₅ powders, which will have promising use in electroceramics.

2. Experimental procedure

The Ta₂O₅ powders were prepared by the controlled hydrolysis of a dilute alcoholic solution of tantalum pentaethoxide, Ta(OC₂H₅)₅ (Kojundo Kagaku Laboratory Ltd., Japan). Ta(OC₂H₅)₅ and double distilled water were separately dissolved in ethanol, *n*-butanol

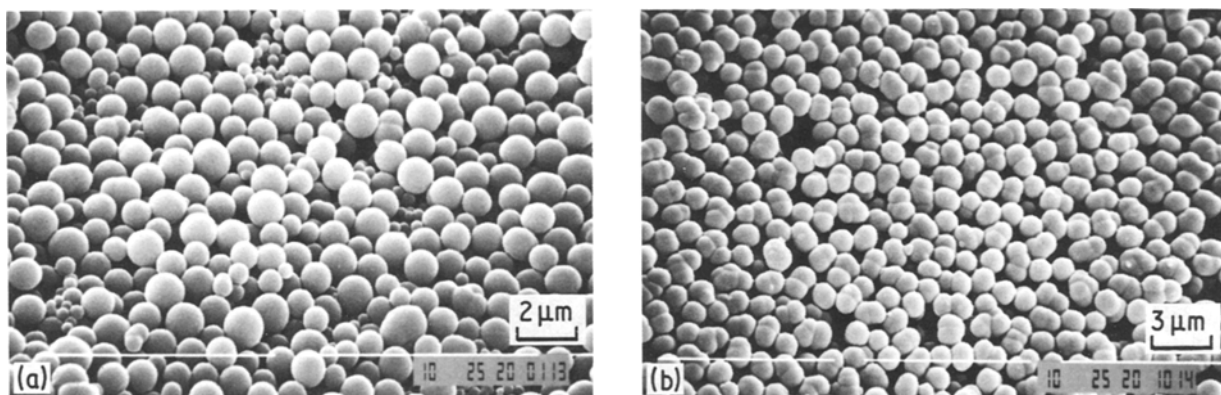


Figure 1 Scanning electron micrographs of monodispersed Ta₂O₅ · *n*H₂O fine particles: (a) mixed alcohol of *n*-butanol and ethanol (vol ratio = 4:1), and (b) ethanol.

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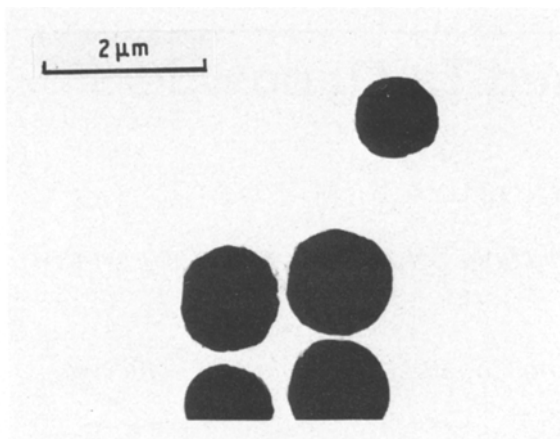


Figure 2 Transmission electron micrograph of monodispersed $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ fine particles.

and a mixed alcohol of *n*-butanol and ethanol, in which (vol ratio = 4:1) addition of ethanol is allowed to increase the solubility of *n*-butanol in water. Alkoxide–alcohol and water–alcohol solutions were mixed by a magnetic stirrer, and gave the final composition of 0.1(mol litre⁻¹) of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and 0.3 to 1.0(mol litre⁻¹) of water. The precipitation of white Ta_2O_5 particles occurred in 30 min at 25°C. After 1 h mixing, Ta_2O_5 particles were separated from the mother liquor by using a centrifugal separator and dried at 60°C.

Particle size and distribution of obtained powders were measured by transmission electron microscope (TEM) (JEM model 200CX, JEOL Ltd., Japan). Particle shape and the state of the agglomerates were evaluated by scanning electron microscope (SEM) (JEM model T200, JEOL Ltd., Japan). The powders were also studied by powder X-ray diffractometry (PW1700 Philips, The Netherlands) and by differential

3. Results and discussion

Fig. 1 shows the typical scanning electron micrographs of Ta_2O_5 particles obtained from the different kinds of alcoholic solutions. In the case of *n*-butanol as the solvent (Fig. 1a), the particles seem to be spherical, and non-agglomerate and also have a uniform size and very narrow size distribution. Fig. 2 shows the transmission electron micrograph of the same particles as shown in Fig. 1a. The particle shape was close to a sphere and had a size of 1.2 μm, which was the same as the SEM observation. While in the case of ethanol (Fig. 1b) the particles have the average diameter of 0.8 μm, but tend to form an agglomerate like a tetrapod or a dumb-bell shape. Fig. 3 is the particle size distribution calculated from the TEM observation. This distribution tends to obey logarithmic normal distribution and has a geometrical standard deviation of about 1.09. For this situation it can be assumed that the particles have almost the same size.

The effect of the water content in *n*-butanol solution on particle preparation was also investigated. Fig. 4 shows the morphological difference of the particles obtained from different water content 0.3 to 1.0(mol litre⁻¹) under the constant concentration of 0.1(mol alkoxide litre⁻¹). In all cases of (a) 3, (b) 5 and (c) 10 for $\text{H}_2\text{O}/\text{Ta}(\text{OC}_2\text{H}_5)_5$ ratio gave spherical particles. However, according to careful observation, the case of (a) seems to have wide size distribution and become the polydispersed state, and the case of (c) forms a strong agglomerate with irregular shape and size.

This evidence suggests that the preparation of monodispersed Ta_2O_5 particles take place within a

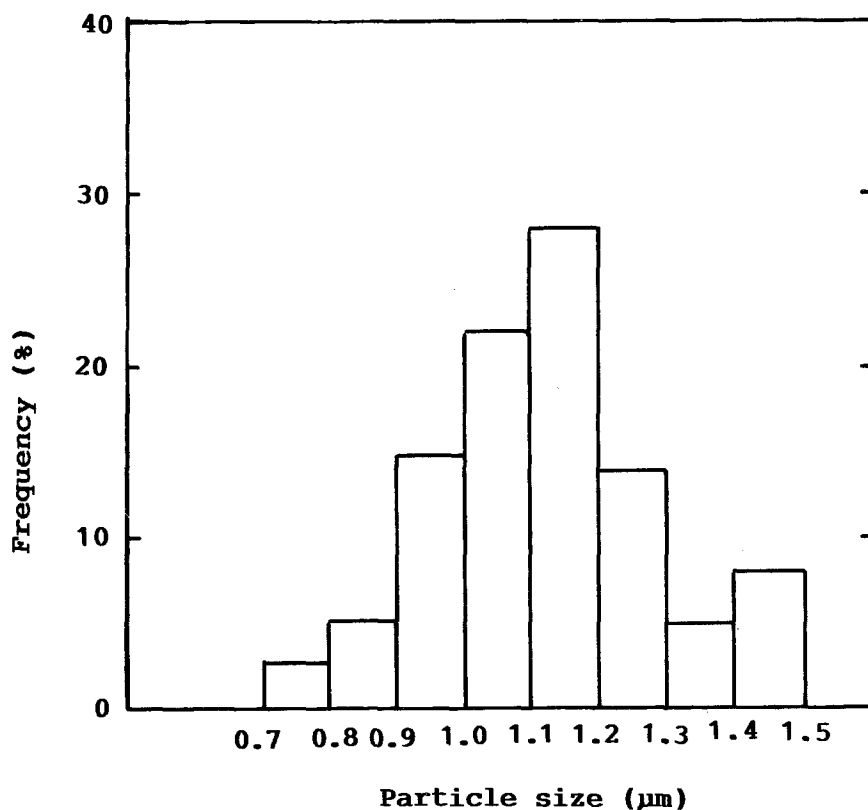


Figure 3 Particle size distribution of $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ fine particles. $\sigma_g = 1.09$, $D_{ave} = 1.2 \mu\text{m}$.

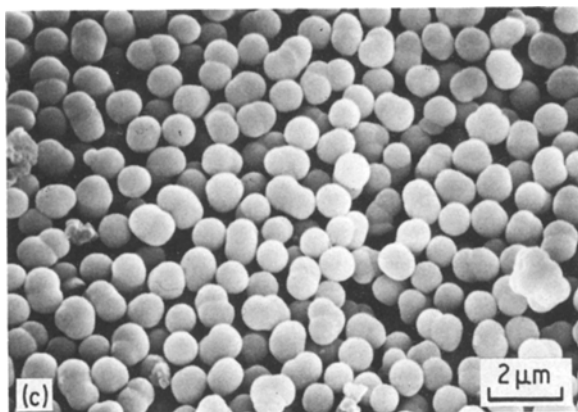
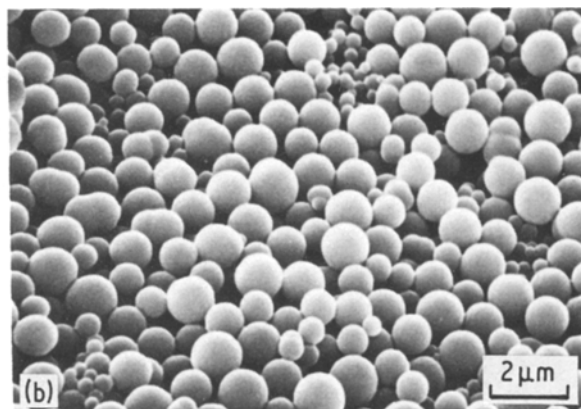
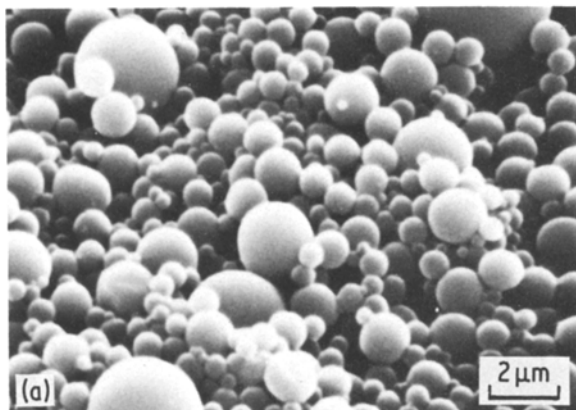


Figure 4 Morphological difference of $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ fine particles for different $\text{H}_2\text{O}/\text{Ta}(\text{OC}_2\text{H}_5)_5$ ratios: (a) 3, (b) 5 and (c) 10.

very limited condition, that is, $0.1(\text{mol litre}^{-1})$ concentration of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and about 5 for $\text{H}_2\text{O}/\text{Ta}(\text{OC}_2\text{H}_5)_5$ molar ratio is required to prepare these particles. Further, the kind of alcohol used as a solvent is also important to disperse and coagulate the particle. Moreover, the very limited concentration range suitable for the preparation also suggests that an electrostatic field around the particles in the solution may be very changeable by other factors. The above phenomena are suggestive of the preparation of

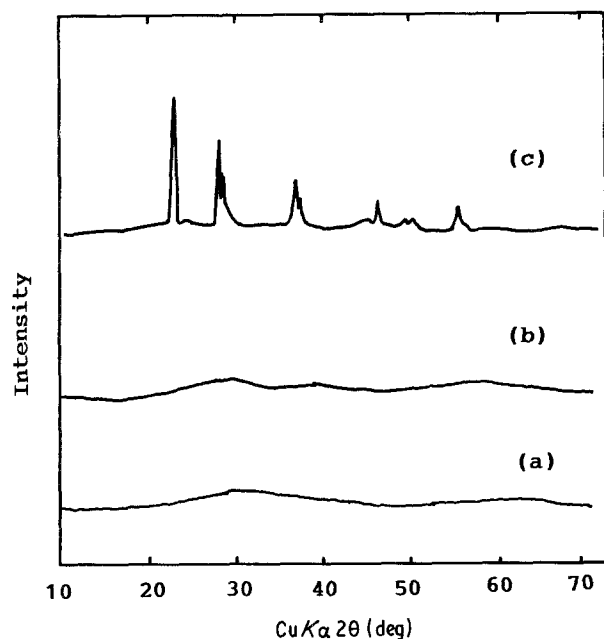


Figure 5 X-ray diffraction patterns of $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ fine particles heated: (a) 60°C (b) 500°C (c) 800°C .

more highly monodispersed Ta_2O_5 particles with high quality.

The as-prepared Ta_2O_5 particle is amorphous and gives no X-ray diffraction pattern (Fig. 5a), for heating from 25 to 500°C . After heating at 800°C , the amorphous particles crystallize to a crystalline oxide which gives the sharp X-ray diffraction patterns of Ta_2O_5 [12]. Thermal behaviour of the particle was studied by DTA–TG techniques. The thermal analytical curves of Fig. 6 show that the particles evolve water corresponding to 15% of their total sample weight with a broad endothermic peak of DTA. The very sharp exothermic peak of DTA at 290°C is due to the combustion of unreacted alkoxy groups, but the amount of unreacted species was not able to be measured exactly by TG, and is apparently, less than 0.1% of the total sample weight. The anhydrous amorphous Ta_2O_5 oxide crystallizes at 740°C with a sharp exothermic reaction and no weight change Fig. 7 shows scanning electron micrographs of monodispersed Ta_2O_5 particles annealed at 500 and 800°C for 2 h. The particles annealed at 500°C were spherical, non-agglomerated, similar to the starting particles and shrank from 1.2 to $1.05\ \mu\text{m}$. Imperfect oxidation of residual organic groups results in the formation of grey coloured particles. Further the particles annealed at 800°C was also spherical, but coagulated loosely, and shrank to $0.96\ \mu\text{m}$. The particle colour also changed from grey to white.

In this way the morphology of monodispersed $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ particles was kept almost the same, through precipitation, drying, dehydration and crystallization. The monodispersed Ta_2O_5 crystalline particles will be promising materials for electroceramics.

4. Summary

1. Monodispersed Ta_2O_5 fine particles were synthesized by the hydrolysis of tantalum pentaethoxide $\text{Ta}(\text{OC}_2\text{H}_5)_5$ in a mixed alcohol of *n*-butanol and ethanol (vol ratio = 4:1).

2. The particles had a spherical shape and were non-agglomerated and grew to $1.2\ \mu\text{m}$ for 1 h after hydrolysis.

3. X-ray diffraction and DTA–TG analysis showed the as-prepared particles were amorphous, hydrated,

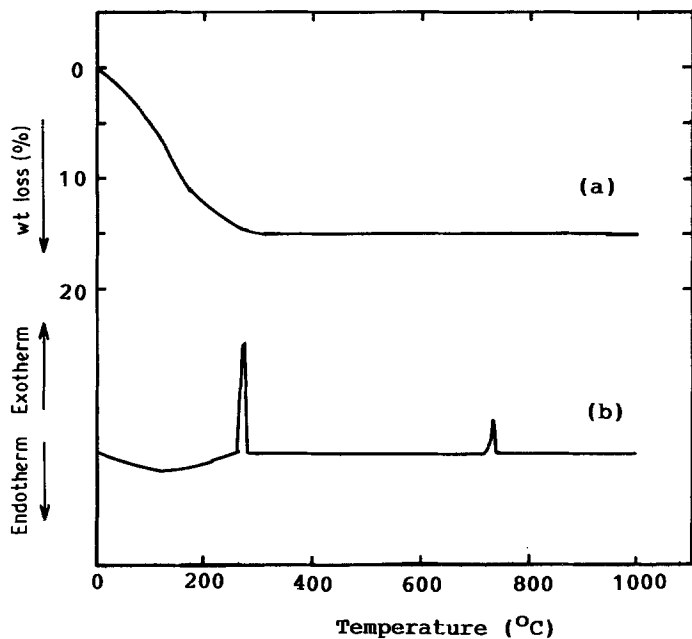


Figure 6 (a) TG and (b) DTA curves of $Ta_2O_5 \cdot nH_2O$ fine particles.

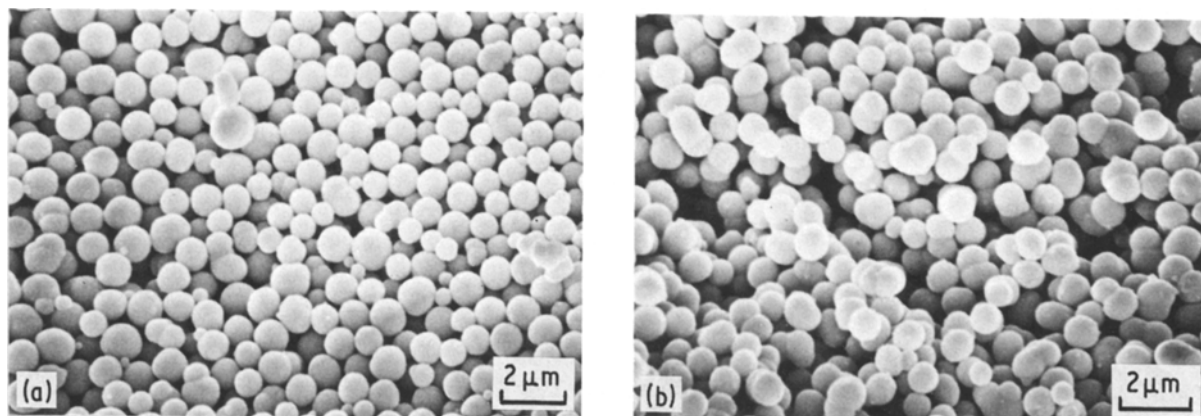


Figure 7 Scanning electron micrographs of monodispersed Ta_2O_5 annealed at (a) 500°C and (b) 800°C for 2 h.

and then gave monodispersed Ta_2O_5 crystalline particles at 740°C.

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