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Oxidative Pulverization of UO_2 Pellets

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Oxidative Pulverization of UO_2 Pellet

Summary

The relationship between the condition of the oxidative pulverization of UO_2 pellet in air and the properties of the resulting powder, U_3O_8, was investigated.

The pellets, sintered in vacuum at 1450°C, were oxidized in air in a muffle furnace at temperatures between 400° and 800°C. The particle sizes distributed over a range less than 10 microns for the powders produced by oxidation at 400° and 500°C, while above 600°C, the distribution tended to spread over a wider range exceeding 10 microns. The surface area of the produced powder decreased with the increase in oxidation temperature.

The surface area of the produced powder decreased when the powder was heated at 700° or 800°C, with no change in the particle size distribution of the powder.

Oct. 1968

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UO_2 ペレットの酸化粉末化

要　旨

ペレット状二酸化ウランを空気中で加熱すると，容易に U_3O_8 まで酸化されると同時にペレットは崩壊し，粉末化することはよく知られている．この現象は乾式再処理法の一つであるフッ化物揮発法の前処理法として有望であり，生成粉末を直ちにつぎの流動層によるフッ素化プロセスに送ることができる．このような観点から，酸化温度により，生成する粉末の物理的特性がどのように変化するかを調べた．実験に使用した二酸化ウランペレットは 145℃ で真空焼結されたもので，96% T. D. の密度を有している．粉末の特性として，密度，比表面積および，粒径分布を測定した．400° および 500℃ の酸化温度では，粒径は 10μ 以下のものが大部分を占めているが，600° から 700℃ の温度範囲では粒径は温度とともに増加するとともに分布の範囲も増加する傾向がある．逆に比表面積は酸化温度とともに減少する．また生成粉末を 700℃，あるいは 800℃ で加熱処理すると比表面積は減少するが，粒径分布は熱処理前のものと同様に保たれることがわかった．

1968年10月

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1. Introduction

The oxidation of UO_2 powder by oxygen has been studied intensively by several investigators.[1)2)3)] In the temperature range below 260°C, UO_2 is oxidized up to $UO_{2.34}$ and its rate is in good agreement with the mechanism controlled by diffusion of oxygen in the solid phase. Above 260°C, UO_2 is oxidized up to U_3O_8 by a two step reaction through the phase of U_3O_7.

For the oxidation of UO_2 pellet, PEAKALL and ANTILL have reported that below 350°C the rate of oxidation is very slow, from 350° to 600°C pellet is oxidized rather quickly to U_3O_8 and is broken into fine particles, and from 650° to 850°C a protective film appears to be formed on the pellet surface.[4)] MUKAIBO, KANNO, and MIKI have investigated that the average particle size of the produced powder increases with the oxidation temperature.[5)] This pulverization behavior has already been considered to be applicable to the oxide fuel reprocessing; i.e., the separation of the nuclear materials from its sheath, and the separation of some fission products.

For the fluoride volatility process, this pulverization may be used as the head end process for the convenience of the next fluorination process in the fluid-bed.

In the fluorination of uranium oxide powders, the surface area, measured by B. E. T. method, is roughly proportional to its reactivity.[5)] On the other hand, the control of the distribution of particle size is an important factor to obtain a good fluidization state.[7)] Considering the above, this work was made to gain some prospective view for making the desired powder by selecting the condition of the oxidative pulverization of UO_2 pellet. The properties of the powders produced under different conditions were compared by measuring the adsorption surface area and the particle size distribution.

2. Experimental Method

2.1 Materials

The two kinds of uranium dioxide pellets, supplied from Mitsubishi Atomic Power Industries Inc., were used; they were in the dimensions, 9 mm diameter, 5 mm long (noted as L) and 6 mm diameter and 2 mm long (noted as S). The densities of both the pellets were in 96% of the theoretical density. They were produced by sintering in vacuum for 2 hours at 1450°C. The impurities in ppm are as follows: Fe, 220; Si, 110; C, 39; Mo, 21; Ca, 20; N, 16; Ti, 15; Al, 14.[8)] The smaller pellets (S) were only used for the preliminary experiments described in section 3.1. The larger pellets (L) were used for all of other experiments.

2.2 Measurement of powder properties

2.2.1 Surface area

Krypton adsorption at liquid nitrogen temperature was measured by B. E. T. method and the adsorption surface area was calculated.

2.2.2 Density of powder

It was measured by the liquid displacement method in a pycnometer. To promote the liquid

impregnation into the pores in the solid phase, the system was evacuated repeatedly until the equivalent values were obtained for the subsequent measurements.

2. 2. 3 Particle size distribution

First, the powder product was sieved with JIS sieves (Japan Industrial Standard), after which the size distribution was measured with an automatic sedimentograph[10] which determines the proportion of particles that have passed the 325 mesh sieve (44 micron in opening size). A solution of sodium hexametaphosphate (0.03 w/o) was used as dispersing medium, in which the sample powder was mixed to an amount of 2 w/o. The concentration of the dispersing agent was determined by a sedimentation test[11] in a glass tubular bottle, 1 cm diameter and 30 cc volume. In this tube, 2 weight % of powder was suspended in 30 cc aqueous medium and the rate of sedimentation was measured for the various concentration of the dispersing agent. **Fig. 1** shows

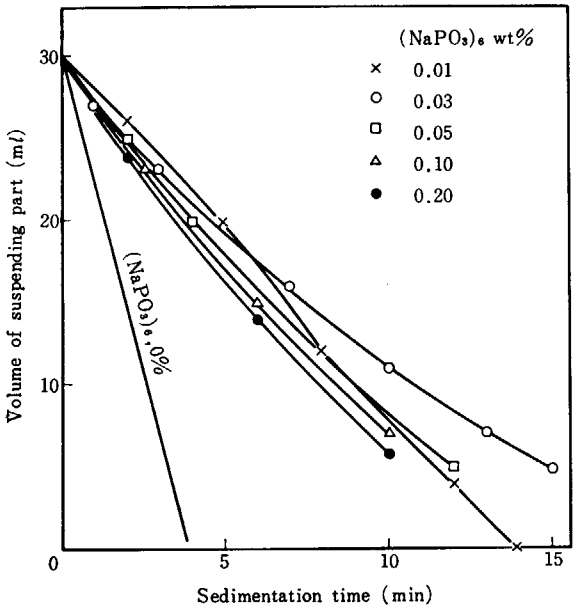


Fig. 1 Effect of the concentration of $(NaPO_3)_6$ on the sedimentation rate of U_3O_8 powder.
U_3O_8 powder was produced by oxidation of UO_2 pellet in air at 500°C for 1 hour.

changes in the suspended volume against time. The suspension was prepared by leaching the powder in the solution for 10 minutes under vacuum and then by stirring mechanically for 20 minutes.

3. Results and Discussion

3. 1 Oxidation behavior of UO_2 pellet in air

As a preliminary, the oxidation behavior of UO_2 pellets was observed for determining the experimental conditions of pulverization. First, the reactor was filled with argon and then set to a reaction temperature. The air (dried by magnesium perchlorate) or oxygen was supplied into the reactor at a flow rate of 15 to 20 *l*/hr. The weight change of the UO_2 pellet was measured by a thermobalance.

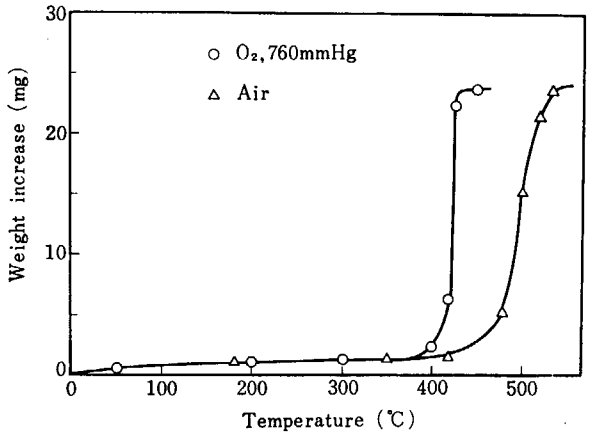


Fig. 2 Weight gain of pellet with increase in oxidation temperature.
UO_2 pellet, 6 mm in dia. and 2 mm in thickness; raising rate of the oxidation temperature, 5°C/min.

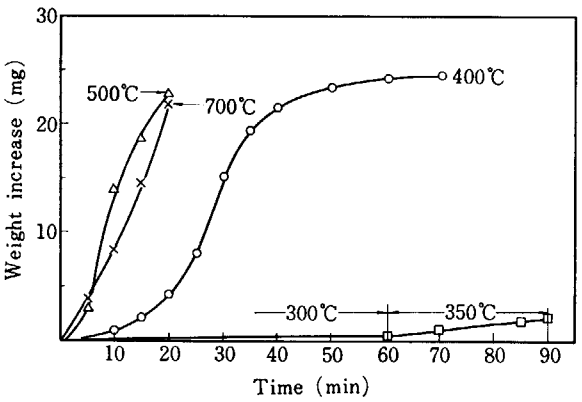


Fig. 3 Weight gain of pellet during oxidation in air at different temperatures.
UO_2 pellet, 6 mm in dia. and 2 mm in thickness.

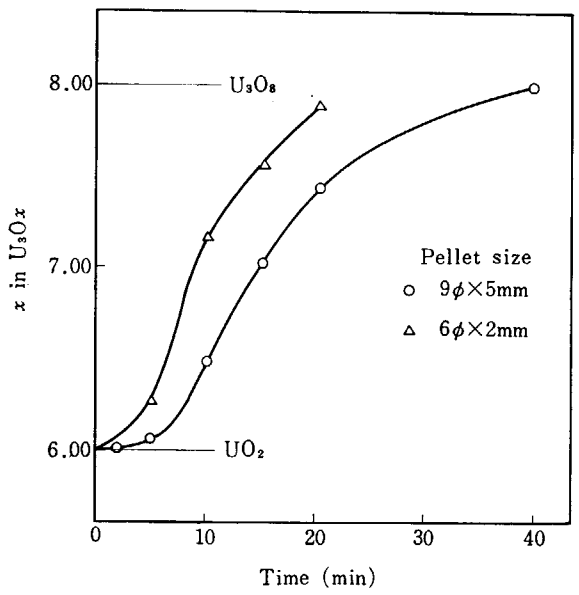


Fig. 4 Oxidation behavior of UO_2 pellet in air—effect of pellet size.
Oxidation temperature; 500°C.

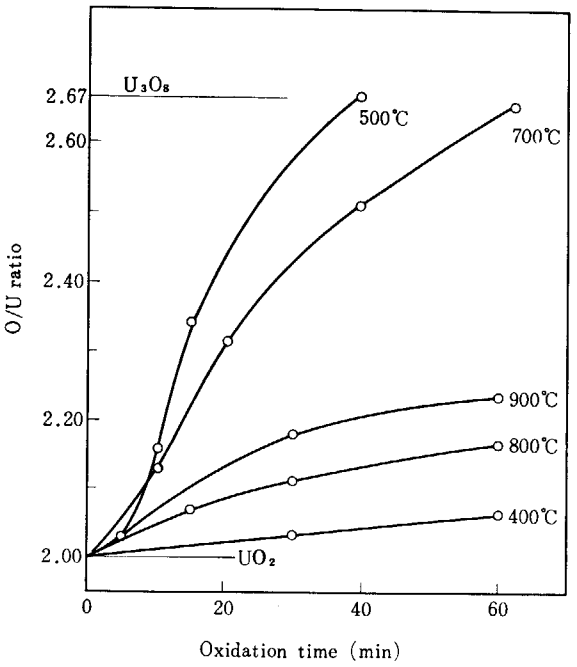


Fig. 5 Oxidation behavior of larger UO_2 pellet in air at different temperatures.
UO_2 pellet, 9 mm in dia. and 5 mm in thickness.

Fig. 2 shows a weight gain curve, which was obtained when the oxidation temperature of the UO_2 pellet was raised at a rate of about 5°C/min. The weight increase due to oxidation began at 450°C. **Figs. 3, 4** and **5** show curves of the typical weight changes of UO_2 pellets in air at different temperatures. At 400°C, the oxidation started after a long induction period. Between 450 and 700°C, the oxidation proceeded rather rapidly, and its rate did not change much with the increase in temperature. Above 700°C, the rate of oxidation tended to decrease, and at 800°C, the rate became very low. The forms of the curves in **Figs. 3** and **5** are much similar to those obtained by PEAKALL and ANTILL. By considering the oxidation behaviors of the UO_2 pellets described above, the pulverization behavior was studied mainly in the temperature range between 500°C and 700°C.

3.2 Preparation of powders and their properties

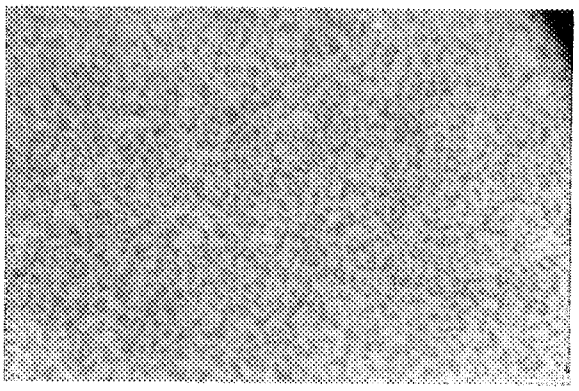
The pellets, put on a silica boat, were introduced into a muffle furnace which had been set to a desired temperature. In any case, the UO_2 pellets were oxidized finally up to U_3O_8. The pulverization occurred with the progress of the oxidation. At temperatures between 500° and 700°C, the oxidation and pulverization were completed within one hour, while at 400°C, three hours was necessary. After the sample was heated, it was cooled as quickly as possible outside the furnace. The properties of the powder produced was not affected with the presence of moisture in air during the oxidation as described later, so that the experiments were made without eliminating the moisture in the air. The powders produced were always in the form of U_3O_8, which was confirmed by X-ray analysis and from the increase in weight after oxidation. The measured densities of powders were also in good agreement with the theoretical value of U_3O_8, 8.39; measured values were 8.39 ± 0.1 as shown in TABLE 1. This result indicates that the each particle

TABLE 1 Densities of the produced powders. Sample powders were produced by oxidation of pellets, 9 mm in dia. and 5 mm in thickness, in air.

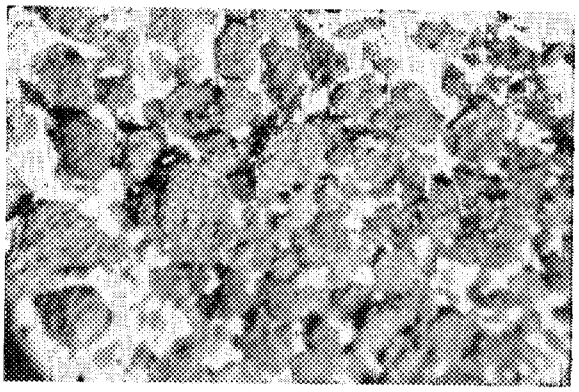
Oxidation temperature	500°C		600°C	700°C
Densities	8.47	8.37	8.31	8.38
	8.32	8.32	8.30	8.33
	8.47	8.32	8.33	8.32
	8.39	8.35	8.34	8.39
	8.39 *	8.42	8.37	8.32
	8.37	8.37	8.26	8.34
	8.32	8.36	8.35	8.33
	8.33	8.38		
	8.36	8.42		
		8.46		
		8.36		
		8.39		
		8.36		

Before measurement of the density, the powder, partly agglomerated, was broken by a mortar excepting the measurements noted by *.

has almost no closed pore and fine crack in itself. The powders formed below 600°C, were voluminous and fine, but the powder produced at 700°C was found to be mixed with many flat lumps, 1 to 2 mm in diameter and less than 1 mm in thickness, in which a stacking structure of thinner layers was seen. At 800°C, the oxidation and pulverization were very slow, so that the form of pellet remained scarcely changed after the sample was heated for one hour. **Photo 1** shows various states of the products. **Fig. 6** shows the particle size distribution for the powders formed at various temperatures. It is seen that the oxidation at lower temperatures produces finer powders with particle sizes, distributed in a narrow range less than 15 microns. On the contrary, for the powder formed at 700°C, the distribution of particle size spreads over a wider range and the fraction of particles more than 44 microns in size are over 40 weight %. From the results shown in **Fig. 6**, it is evident that the pulverization proceeds most effectively at 500°C; in the temperature range from 450° to 550°C, the oxidation rate and the size distribution of the produced powder were nearly invariable. The fact that the particle size of produced powder tends to increase with the rise of oxidation temperature, is in good agreement with the result reported by MUKAIBO, *et al.*[6]



A



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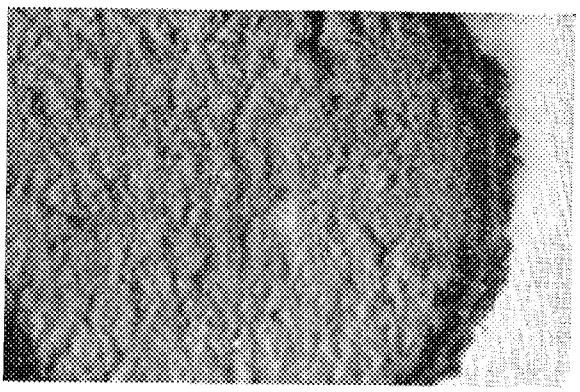

C

Photo 1 Photographs of the product formed by oxidation at different temperatures (×10)

A: U_3O_8 fine powder produced by oxidation at 500°C for 1 hour

B: U_3O_8 lumps produced by oxidation at 700°C for 1 hour

C: Surface of the pellet after oxidation at 800°C for 1 hour

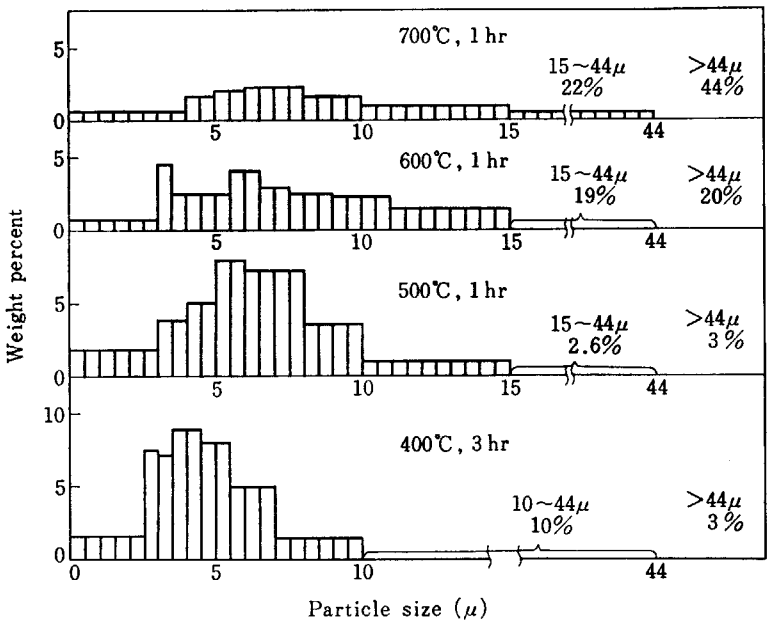

Fig. 6 Effect of oxidation temperature on particle size distribution. Powders were produced by oxidation of UO_2 pellet, 9 mm in dia. and 5 mm in thickness, in air.

3.3 Surface area of powder

The surface area of the powder determined by adsorption of Kr decreased with the rise of the oxidation temperature as shown in **Fig. 7**. By supposing that each particle is spherical with no crack and no geometrical irregularity, the surface area of powder can be calculated from the result of the particle size distribution. This value was calculated to be 0.15 m^2/g for a powder produced at 500°C, while the surface area determined by adsorption of Kr for the same powder

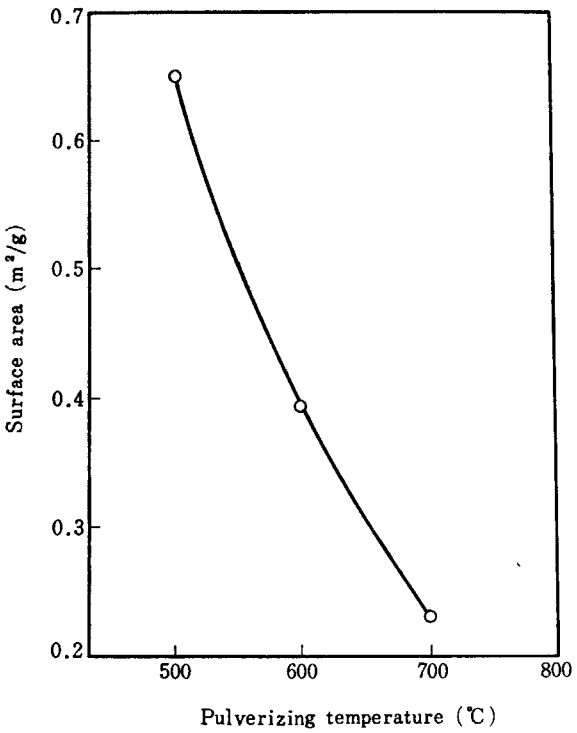

Fig. 7 Dependence of surface area of produced powders on their oxidative pulverization temperatures.

was about 4 times (0.62 m^2/g) as large; this difference appears to show the degree of the surface irregularity.

A powder produced with the oxidation at 500°C, having a surface area of 0.62 m^2/g, was heated to 700° or 800°C in air for one hour respectively. **Fig. 8** shows that the surface area of the powder is readily decreased by this heat treatment whose temperatures are much lower than the decomposition temperature of U_3O_8, 1450°C.[15] However, the particle size distribution was not

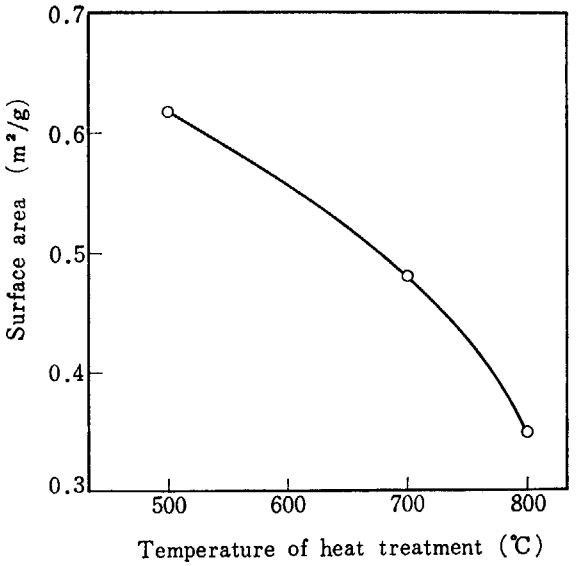

Fig. 8 Reduction of the surface area of produced powder by heat treatment of powder.
Heat treatment of powder, 1 hour in air. Plot at 500°C corresponds to the surface area of the original powder produced by oxidation of UO_2 pellet (L) at 500°C for 1 hour.

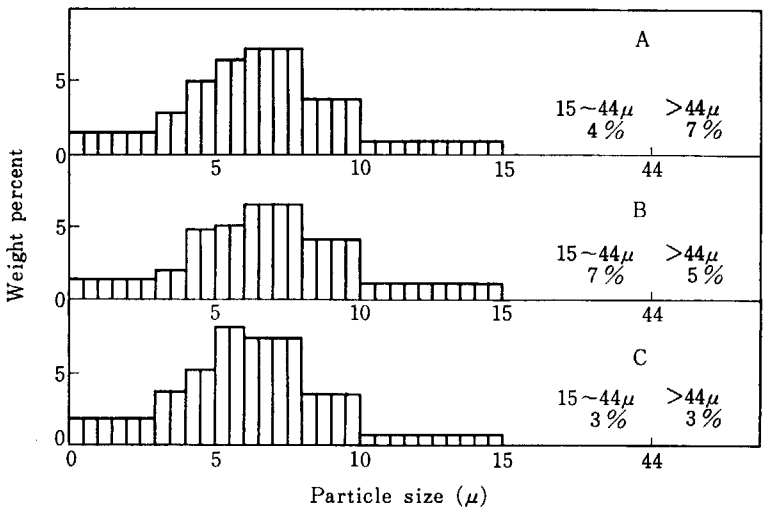

Fig. 9 Size distribution of powder after heat treatment.
A: Original powder C was heat treated at 800°C for 1 hour
B: C was heat treated at 700°C for 1 hour
C: Original powder produced by oxidation of UO_2 pellet (L) at 500°C for 1 hour.
Atmosphere in heat treatment; air.

changed by the above heat treatment as shown in **Fig. 9**. These results suggest that the decrease in surface area is due to the reduction of the surface irregularity on each particle and not due to the sintering among the particles. It can further be supposed that all the particles are fully separated each other and not in the agglomerated state. If not so, resintering of the pulverized

powder would easily occur. By appropriately choosing the conditions of the oxidation of UO_2 pellet and of the heat treatment of the resulted powder, it may be possible to obtain the powder having the desired properties regarding the size distribution and surface area.

3.4 Effect of moisture on the pulverization

Several experiments were made to confirm the effect of moisture on the particle size distribution; i.e., UO_2 pellets were oxidized at 500°C in a stream of air dried by magnesium perchlorate, or in a stream of air saturated with moisture, at air flow rate of 10~15 *l*/hr. The results showed that the presence of moisture did not influence the particle size distribution of the produced powder.

3.5 Oxidation of pellet in pure oxygen

A little difference was seen in the particle size distribution between the powders formed by oxidation in air and in oxygen. **Fig. 10** shows the particle size distribution of the powders formed by oxidation in pure oxygen. The pellet was not broken by one hour oxidation in air at 800°C, whereas it was broken in oxygen (1 atm.), although the sizes of the resulting powder particles were

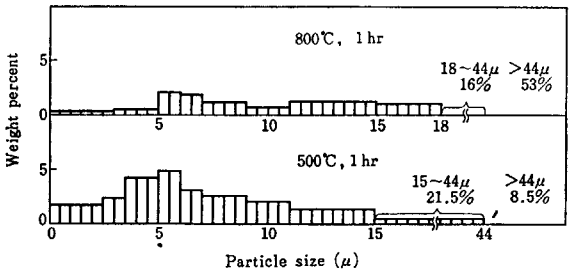

Fig. 10 Size distribution of powder produced by oxidation of UO_2 pellet in pure oxygen (1 atm).
UO_2 pellet, 9 mm in dia. and 5 mm in thickness.

not fine as shown in **Fig. 10**. The pulverization of the pellet in oxygen occurred acceleratedly above 400°C, while it began to occur at a somewhat higher temperature of 450°C in air. From these results, the temperature range of the pulverization in oxygen seems to be a little wider than that in air. The sizes of the particles formed in oxygen at 500°C (**Fig. 10**) are larger than those of the particles formed in air (**Fig. 6**); the oxidation rate of the UO_2 pellet increases with increase in the partial pressure of oxygen, and the resintering of the produced powder, U_3O_8, seems to occur partly.

4. Conclusion

The relationships between the conditions of the oxidative pulverization of UO_2 pellet in air and the properties of the resulting power, U_3O_8, were investigated. The powder properties were compared by measuring the adsorption surface area and the size distribution.

The temperature dependence of the oxidation of UO_2 pellet was as follows:

at 400°C, oxidation proceeded after a long induction period;

at 450° to 700°C, it proceeded fairly rapidly;

at 800°C, it proceeded at a very low rate.

As the oxidation temperature was raised, the particle size distribution spreaded over a wider range and the surface area of the powder decreased.

The surface area of the produced powder was reduced by heating the powder at a temperature within the range from 700° to 800°C, while the size distribution of the powder was not changed by this heat treatment.

The powder having desired size distribution and surface area may be prepared by appropriately choosing the conditions of oxidative pulverization and the succeeding heat treatment.

Acknowledgement

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