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Effect of UO_{2+x} Powders Produced at Different Oxidation Temperatures on the Properties of Pellet

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ABSTRACT

Characteristics of UO_{2+x} powders oxidized at different temperatures were examined. Pellets were fabricated by adding these oxidation powders and their properties were also investigated. Particle size of the UO_{2+x} powders decreased with increasing oxidation temperature while surface area increased. Only the powders oxidized at 350°C enhanced the strength of green pellet. However, 350°C oxidized powders added pellet had many surface defects. The difference of shrinkage rate between the oxidized and UO_2 powders was thought to be the cause of them.

Key words : UO_2 pellet, U_3O_8, Green strength, Oxidized powder

1. Introduction

UO_2 pellets used as a fuel for nuclear power plant are manufactured through a series of consecutive processes. The compaction step is the key process in determining the surface integrity of sintered pellet. Among many factors affecting the surface quality of the pellet, green strength plays a decisive role. In general, binders have been used to enhance the green strength of the pellet, but its use in a mass production line has many problems, such as requiring an additional dewaxing furnace to evaporate binders and limiting production capacity due to criticality problem. It has been known[1] that the green strength can be increased by the addition of U_3O_8 powder. About 10 wt% of U_3O_8 powder is added to the homogeneous UO_2 powder in the commercial line. In terms of manufacturing cost, the addition of U_3O_8 powders is quite significant because they are made from pellet scraps. U_3O_8 powders reduce the sintered density by forming small pores. A density drop effect of U_3O_8 powders is very important because UO_2 pellet must meet the requirement of the specification. Since U_3O_8 powder acts as a small pore-former, excess addition of U_3O_8 powders by more than 10 wt% has a detrimental effect on the thermal stability resulting from the segregation of small pores that lead to inhomogeneous densification of pellets.

Because of these reasons, an alternative method for improving the green strength has been considered. FRAGEMA had a patent about increasing green strength by adding oxidized powder made from virgin UO_2 powder instead of pellet scrap.[2] The green pellet strength can be increased by the addition of the oxidized powder but it formed many surface defects. It is not yet explained why these surface defects occur. In this work, we prepared the oxidized powders produced at different temperatures and examined their characteristics to investigate the possibility of being used as an additive for improving the green strength. Properties and microstructural changes of the pellet containing the oxidized powder are also examined. A possible mechanism on how to create the surface defect has been suggested based on these results.

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2. Experimental

2.1. Preparation of the Oxidation Powders

UO_2 powder produced from dry conversion process[3] was used in this study. Characteristics of the UO_2 powder are shown in Table 1. UO_2 powders were oxidized in a box furnace at the temperature range from 150 to 500°C for 4 h in air.

2.2. Pelletizing

In order to evaluate the effect of the oxidized powders on the pellet properties, especially green strength, the same amount of the oxidized powders produced at the different

Table 1. Characteristics of ex-DC UO_2 Powders

Characteristics	Value
Mean powder size (μm)	4.75
Specific surface area (m^2/g)	2.25
O/U ratio	2.007
Bulk density (g/cm^3)	1.7

temperatures were added to each specimen. U_3O_8 powder oxidized from pellet scrap, AZB (**AZ**odicar**B**onamide) as a pore former and ACRAWAX ($H_{35}C_{17}COHNC_2H_4NHCOC_{17}H_{35}$) as a lubricant were also added to mixed powder as much as 8, 0.3 and 0.25 wt%, respectively. Mixing was carried out for 1.5 h in "Turbula Mixer". Standard powders containing 12 and 8% U_3O_8, representing the current manufacturing process, without the addition of the oxidized powders were prepared to compare.

The mixed powders were pressed to have green density of 5.90±0.05 g/cm^3 and then sintered at 1740°C for 5 h. The furnace was heated at the rate of 5°C/min and held at 700°C for 1 h to burn the lubricant out. A pure hydrogen gas was blown to keep the interior of the furnace in a reducing atmosphere.

2.3. Measuring Properties

Characteristics of the oxidized powders such as specific surface area, O/U ratio and mean particle size were measured. XRD (X-Ray Diffraction) experiments were conducted on the oxidized powders to examine phase changes according to the oxidation temperatures. XRD tests were carried out using monochromatic Cu-Kα radiation at a speed of 4°/min. Strength of the green pellets was measured. The pellet for measuring the green strength were carefully selected to exclude other possible factors affecting the property. After sintering, all specimens were ground in order to observe the surface integrity of the pellets.

Sintered density was measured by an immersion method. In all cases the densities were reported as a percentage of the theoretical density of UO_2 (10.96 g/cm^3). One pellet from each condition was sectioned longitudinally and polished to observe its microstructure. For measuring grain size, thermal etching was performed at 1250°C for 1.5 h. Grain size was determined by a linear intercept method.

3. Results

3.1. Characteristics of the Powders Oxidized at Different Temperatures

The variations of mean particle size and specific surface area of the powders as a function of the oxidation temperatures are presented in Fig. 1. Average particle size decreases with increasing oxidation temperatures, while specific surface area increases. As UO_2 powders manufactured by the dry conversion process have quite a number of surface cracks,[1] they are crushed if thermally agitated. The mean particle size of the powder was reduced to 3.05 μm from 4.74 μm when they were oxidized at the temperature of 350°C. There was no particle size change at temperatures higher than 350°C. Fig. 2 shows the results of the green strength of the pellets pressed from powders including the oxidized powders. All the test specimens were made at the same conditions and we selected the pellets which have the same dimension and green density in order to exclude other factors that might affect the green strength.

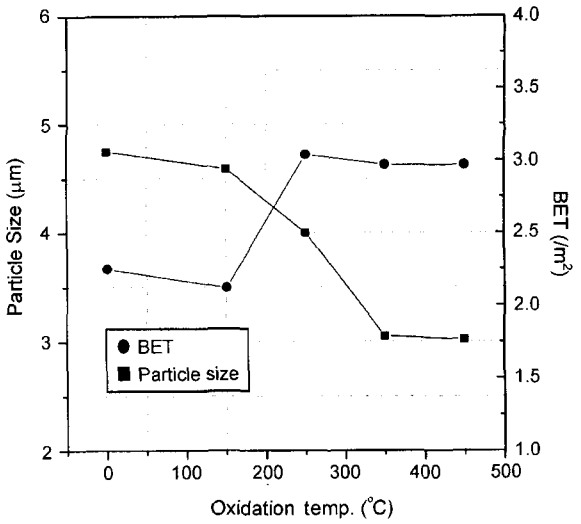

Fig. 1. Variation of particle size and surface area of powders with oxidation temperature.

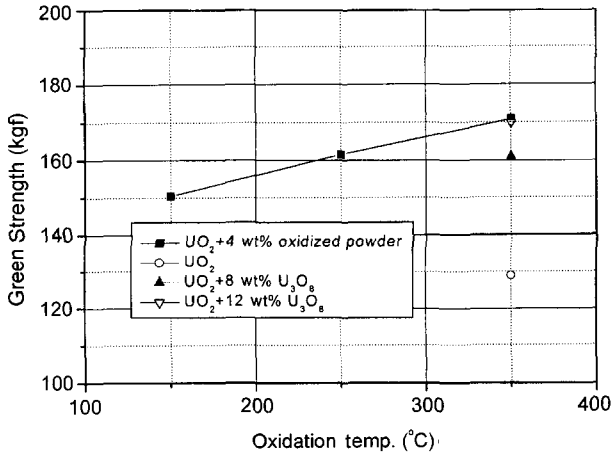

Fig. 2. Variation of green pellet strength depending on the addition of powder oxidized at different temperatures.

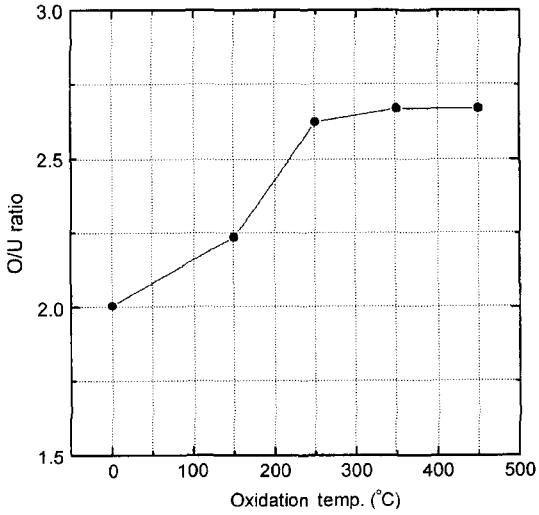

Fig. 3. Variation of O/U ratio of powders with oxidation temperatures.

There is no big difference between the green pellet containing the powder oxidized at both 150 and 250°C and the standard pellets containing 8 wt% U_3O_8. However, the addition of powders oxidized at higher than 250°C seems to have an effect on increasing the green strength of the pellet. As can be seen in Fig. 2, the green pellets containing 4 wt% powder oxidized at 350°C have a similar strength as the standard pellets containing 12 wt% U_3O_8 made from pellet scrap. It is thought that such a result might be related to O/U ratio of the powder. Fig. 3 shows the variation of O/U ratio of the powders depending on the oxidation temperatures. It reveals that the powders should have higher O/U ratio than a certain value in order to act as a promoter of increasing green strength. The O/U ratio of the powders did not change when they were oxidized at the temperature higher than 350°C. It is known[4] that crystal structure of UO_2 is transformed from cubic to orthorhombic through the transition structure of tetragonal depending on the oxidation temperature. But, the accurate transformation temperature can not be attained since it strongly depends on the experiment conditions. The results of XRD (X-Ray Diffraction) experiment on the powders oxidized at the different

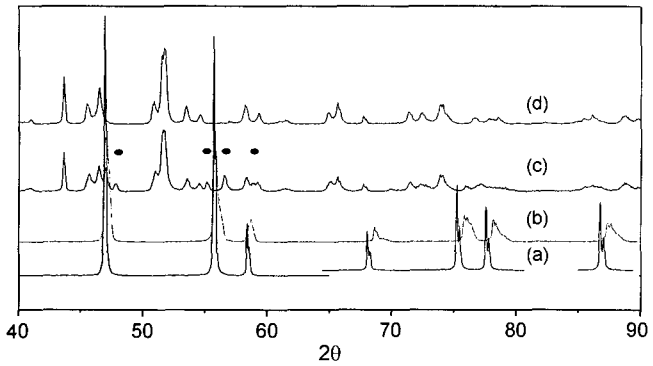

Fig. 4. X-ray diffraction patterns of oxidized powders. (a) virgin UO_2, (b) 150°C, (c) 250°C(●:U_3O_7), and (d) 350°C.

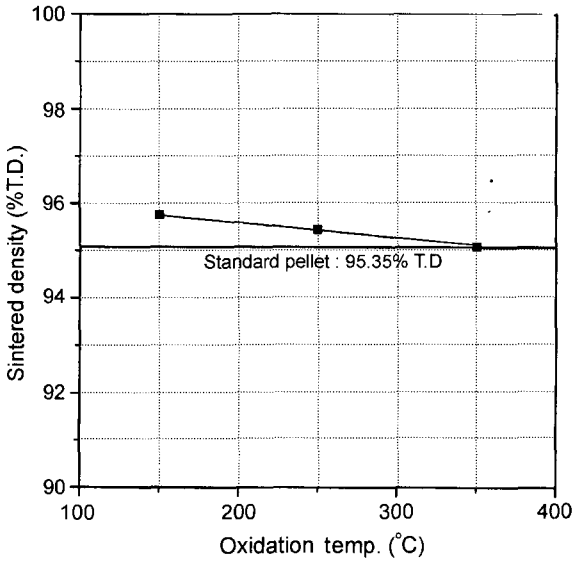

Fig. 5. Variation of sintered density with addition of powder produced at different oxidation temperatures.

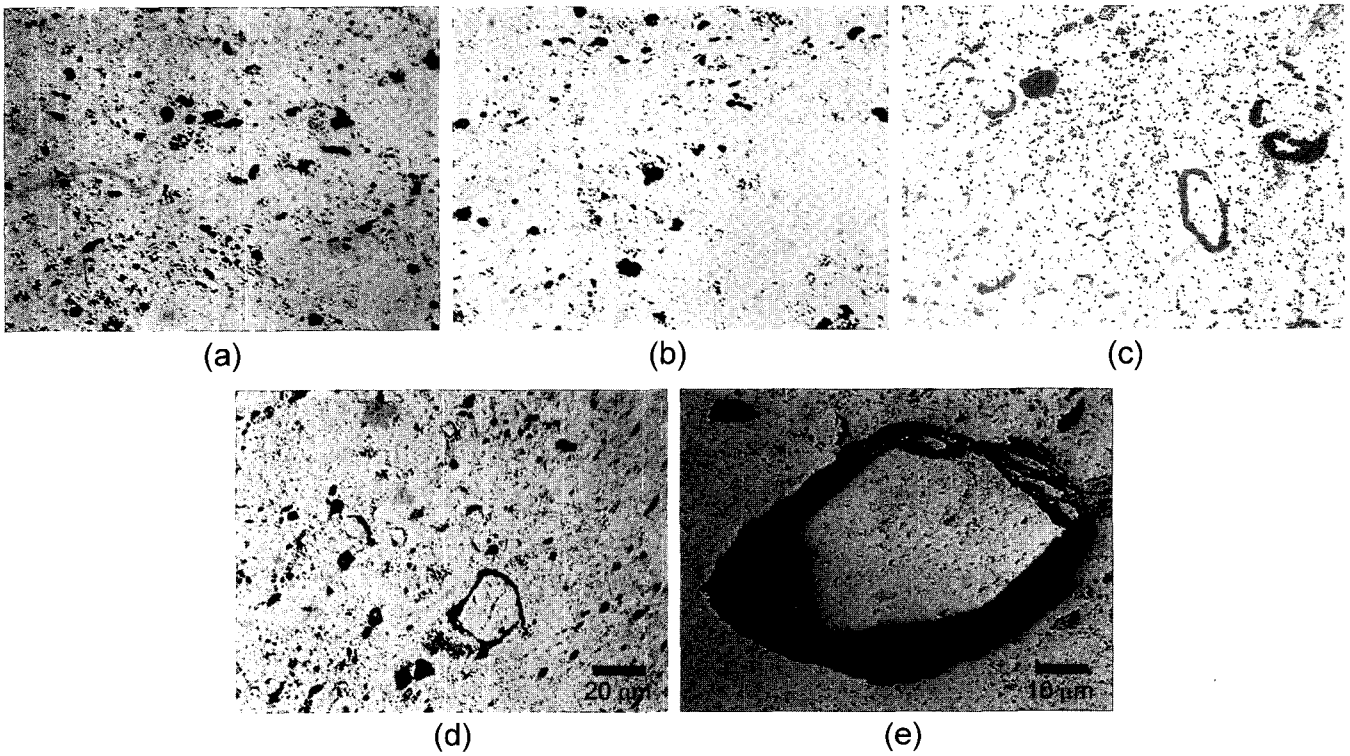

Fig. 6. Microstructural changes of pellets due to addition of oxidized powder. (a) UO_2 pellet(×200), (b) 150°C(×200), (c) 250°C(×200), (d) 350°C(×200), and (e) 350°C(×500).

temperatures are shown in Fig. 4. The UO_2 powder was transformed to U_4O_9 phase at 150°C and changed to U_3O_8 at higher than 250°C. It can be identified that some fraction of U_3O_7 phase existed together with U_3O_8 phase when UO_2 powder was oxidized at 250°C.

3.2. Property Changes of the Sintered Pellet Due to the Addition of the Oxidized Powders

Fig. 5 shows the variation of sintered density of the pellets depending on the type of oxidized powders added. Different from the other pellets, the 150°C oxidized powders added pellet showed slightly higher sintered density than the others. It seems to be related to the phase of the oxidized powder. As mentioned earlier, the 150°C oxidized powders have a U_4O_9 phase whose theoretical density is higher than U_3O_8. In case of the 250°C oxidized powder which has U_3O_7 and U_3O_8 phases simultaneously, its effect on density is small despite of the presence of U_3O_7 phase. The 350°C oxidized powder added pellet has a similar density as that of the standard pellet. Different from the other pellets, 350°C oxidized powder added pellet had large defects as shown in Fig. 6. The defects are appeared as large holes with spherical shape and the largest are greater than 100 μm in diameter. These defects are found in isolated area.

4. Discussion

The strength of green pellets is determined by cohesive force of powders. Powder characteristics such as size, specific surface area and its phase are the major factors affecting the cohesive force. The structure of UO_2 powder[4-7] is transformed from cubic(UO_2) to orthorhombic(U_3O_8) through the transition phase of tetragonal(U_4O_9) depending on the oxidation temperature. As can be seen in Fig. 2, only the oxidized powders having the U_3O_8 phase contribute to enhance the green strength. The green pellet containing the powders oxidized at 150°C shows similar strength to the 8 wt% U_3O_8 added pellet while it increases with the addition of 350°C oxidized powder. The O/U ratio of powders seems to be directly related to green strength property since strength increase can only be observed in green pellets including powders with U_3O_8 phase (see Fig. 3). The 150°C oxidized powders with U_4O_9 phase do not play a role in improving green strength property. Surface[1] oxidation of powder produced by the dry conversion process redivides the grains into jagged aggregates with intertwining ramifications. This powder morphology assists particles to interact with surround particles more strongly and it leads to increase the cohesive force between the particles. In order to make for UO_2 particles having such a morphology, the oxidation temperature should be higher than 350°C where powders are totally transformed to U_3O_8 phase. However, the sintered pellets in which 350°C oxidized powders are added have a lot of defects as shown in Fig. 6. The particle size of oxidized powders decreases with increasing oxidization temperature while the specific surface area increases.

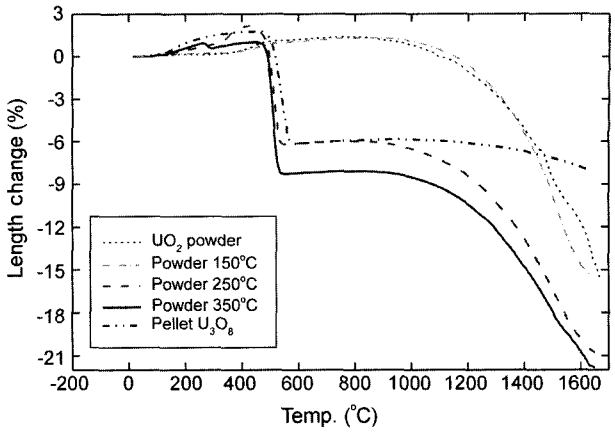

Fig. 7. Results of dilatometer experiments on powders produced at different oxidation temperatures.

The U_3O_8 powders oxidized at 350°C is so active that they will shrink more rapidly than UO_2 powders during sintering (Fig. 7). This is confirmed by dilatometer experiment on the oxidized powders. UO_2 and 150°C oxidized powder show similar contraction behavior during firing and most of the shrinkage occurs at a temperature of over 1100°C. On the other hand, powders oxidized at 250, 350°C and powders made from pellet scrap begin to shrink around 500°C and the shrinkage rate of the 350°C oxidized powder is faster than the other two powders. It is thought that the defects showed in the 350°C oxidized powder added pellet are ascribed to the difference of shrinkage rate of powder during sintering. The 350°C oxidized powders in the matrix are contracted in the early stage of sintering while UO_2 powders start to shrink when shrinkage of the oxidized powders is nearly finished. The shrinkage rate difference between the oxidized powder and UO_2 matrix powder accounts for the defects as shown in Fig. 6.

5. Conclusions

The characteristics of the powders depending on the oxidization temperatures and the properties of pellet containing oxidized powder have been observed. The particle size of powder decreases with increasing oxidation temperature while surface area increases. Through the XRD experiments, it is confirmed that UO_2 powder is completely transformed to U_3O_8 at 350°C through transition phases, U_4O_9 and U_3O_7 at 150, 250°C, respectively. In case of pellets containing the 350°C oxidized powders, defects are found in selected areas. They are not observed in the 150 and 250°C oxidized powder added pellet. The difference of shrinkage rate between added oxidized powder and UO_2 powder is believed to be the cause of these defects. This is identified by the dilatometer experiment.

Acknowledgements

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