

# Reduction behavior of $U_3O_8$ in Ar and $CO_2$ gas atmospheres

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## 1. Introduction

The kinetic study of  $U_3O_8$  reduction to  $UO_2$  in hydrogen atmosphere has already been made and a comprehensive model has been proposed<sup>1,2</sup>. In that model, the nucleation process of  $UO_2$  is instantaneous and the rate-limiting step of growth process is located at the external interface. This means that the hydrogen-oxygen reaction at the surface determines the reduction kinetics of  $U_3O_8$  in the hydrogen containing gas atmosphere.

The reduction kinetics of  $U_3O_8$  in the Ar or  $CO_2$  atmosphere is expected to be quite different from that in hydrogen because the hydrogen-oxygen reaction is not possible in those atmospheres. The oxygen diffusion to and desorption from the surface may control the reduction kinetics in Ar and  $CO_2$ .

In this study, the reduction behavior of  $U_3O_8$  green pellet in Ar and  $CO_2$  at high temperatures between 1100~1400°C was investigated using the thermal gravimetric analysis method. The morphological characteristics of sintered pellet correlated with reduction state were also examined.

## 2. Experiments

The  $U_3O_8$  powder was obtained by oxidation of ADU- $UO_2$  powder at 400 °C in air. The  $U_3O_8$  powder was pressed into green pellets under the pressure of 3 ton/cm<sup>2</sup>.

Green pellets were subsequently heated to the intended temperatures in Ar,  $CO_2$  and  $H_2$  at a rate of 5K/min and isothermally maintained for several hours. The weight changes of green pellets in the course of the heat treatments were monitored by TGA (TG-50, Shimadzu). The sintering of green pellets took place during the TGA experiments. The microstructures of polished section of sintered pellets were observed with an optical microscope. The detailed morphology of fractured interface of pellets was investigated by SEM.

## 3. Results

### 3.1. Reduction kinetic curves (TGA result)

Fig. 1 shows the average O/U ratio changes of  $U_3O_8$  green pellets by the various heat treatments and flowing gas conditions. The O/U ratio was calculated from the weight change. In  $H_2$  gas flowing condition, the O/U ratio began to decrease abruptly at about 400 °C and the

reduction to  $UO_2$  phase is completed at about 600 °C. This result is consistent with other experimental data and well interpreted by a model of nucleation and anisotropic growth from surface to core of  $UO_2$  phase.

In Ar or  $CO_2$  gas flowing conditions, the reduction kinetic curves have different shapes. The temperatures where the O/U ratio started to decrease were shifted to higher temperature of about 600 °C. The reduction progresses very slowly above this temperature. Especially, in the sample, heat-treated at 1100 °C in Ar, the reduction was stopped at the O/U ratio of about 2.61 even the isothermal annealing at 1100 °C for 4h. O/M ratio of 2.61 almost corresponds to the phase limit of orthorhombic  $U_3O_8$ . The oxygen partial pressure of Ar is much lower than the equilibrium oxygen partial pressure of  $U_3O_8$  phase. That is,  $U_3O_8$  at 1100 °C in Ar is not a stable phase and should be converted to a phase having properly lower O/U ratio. Therefore, stopping the reduction at the O/U ratio of 2.61 indicates that nucleation of reduction phase is difficult to initiate at 1100 °C.

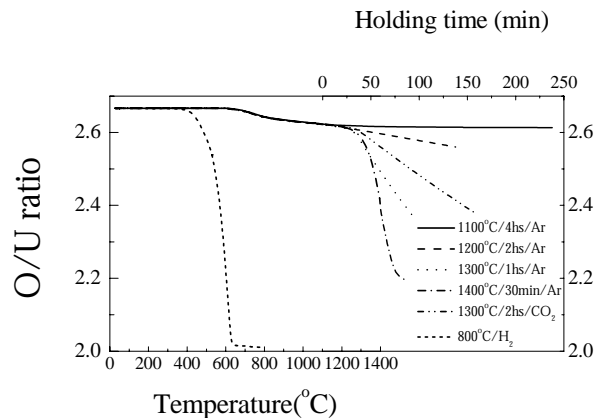


Fig. 1. O/U ratio changes according to various annealing conditions.

When the temperature was elevated to 1200°C, the O/U ratio was linearly decreased with holding time under the isothermal annealing. The reduction rate was accelerated by an increase of annealing temperature. Fig. 2 shows the dependence of rate of O/U ratio change with time on isothermal annealing temperature in Ar. The reaction rate,  $(d(O/U)/dt)$ , well follows the Arrhenius-type dependence on temperature with single activation energy, which indicate that the reduction of  $U_3O_8$  in Ar

atmosphere is a thermally activated process. The activation energy was calculated to be 390kJ/mol.

The reduction rate decreased when the flowing gas was changed from Ar to CO<sub>2</sub> (Fig. 1). It may be closely related with the oxygen potential difference between Ar and CO<sub>2</sub>.

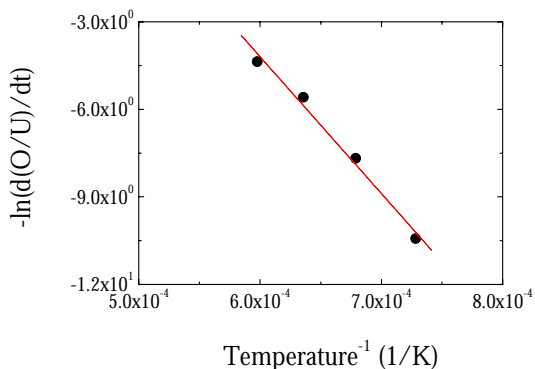


Fig. 2. Isothermal reduction rate dependence on annealing temperature.

### 3.2. Microstructure change of sintered pellets.

Fig. 3 shows the optical microstructure of sintered pellet obtained after the TGA experiments in Ar atmosphere. The pellet from 1100 °C annealing shows the dense and plane microstructure. Where as, when the annealing temperature increased, the second phase was nucleated at the surface of pellet (Fig. 3(b)). The second phase grows from surface to center of pellet, and interface between the inner and outer phases is almost parallel to surface (Fig.3(c)). The contour of Fig. 3(d) reveals that the grain of the second phase has columnar shape, which grows perpendicular to the surface. The sintered sample at 1400 °C shows the columnar grain structure in a almost whole region of pellet.

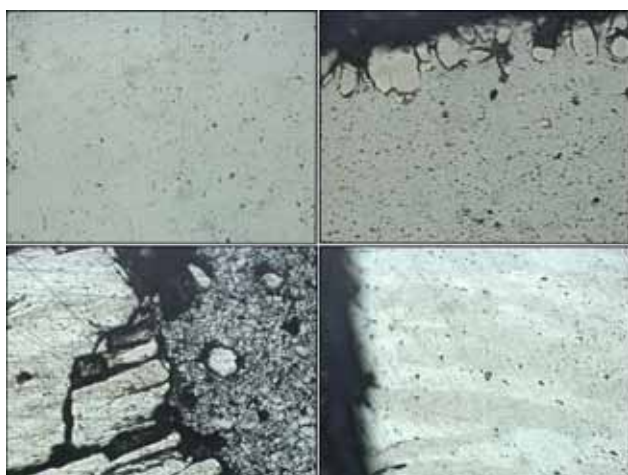


Fig. 3. Microstructure change according to the TGA experimental conditions. The flowing gas is Ar. (a) 1100 °C (b) 1200 °C (c) 1300 °C (d) 1400 °C

The SEM investigation was adopted to observe the detailed microstructure of fractured surface of pellet obtained by annealing at 1300 °C in CO<sub>2</sub>. Fig. 4 shows

the SEM image obtained near the phase boundary. The columnar grains are clearly shown in outer part from interface. Inner part from interface has equiaxed grain structure.

The similar columnar grain structure has been observed in the sintering of overstoichiometric UO<sub>2+x</sub><sup>3</sup>. The columnar structure in that system had been interpreted in terms of surface diffusion assisted by evaporation and condensation process of U<sub>3</sub>O<sub>8</sub> phase. However, the very fast growth of columnar grain is difficult to be simply explained by evaporation and condensation process. The chemical state and crystal structure of second phase are not clear at present. However, the structural different and consequent lattice strain between two phases seems to play a more important role in abnormal grain structure evolution.

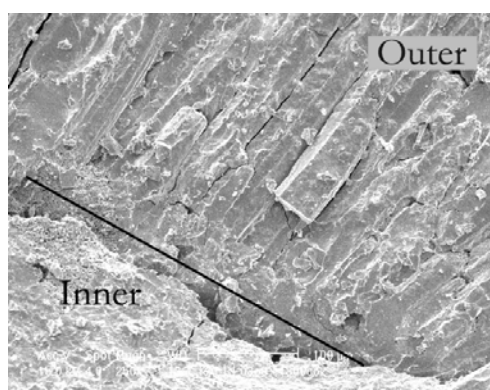


Fig. 4. Morphology of fractured surface of pellet obtained by annealing at 1300 °C in CO<sub>2</sub> gas.

## 4. Conclusion

The reduction of U<sub>3</sub>O<sub>8</sub> green pellet in Ar and CO<sub>2</sub> at high temperature was investigated. The reduction of U<sub>3</sub>O<sub>8</sub> phase started between 1100 and 1200°C. Above this temperature, the O/U ratio linearly decreased with isothermal holding time. The reduced phase has an abnormal columnar type grain structure. This phase rapidly grows from the surface to center.

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