

## ◀Original▶ A Study of Activated Sintering Mechanism of $\text{UO}_2$ Powder by High Temperature X-Ray Diffractometry

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### Abstract

The mechanism for activated sintering of  $\text{UO}_2$  by an addition of 0.05 w/o  $\text{TiO}_2$  was investigated using a high temperature X-ray diffractometer.

The diffraction pattern of  $\text{UO}_2$  pellets was studied in a temperature range from room temperature to  $1200^\circ\text{C}$  in hydrogen atmosphere.

At  $1200^\circ\text{C}$ , the expansion of  $\text{UO}_2$  lattice were 1.448% and 1.354% greater when it was compared with those at room temperature for pellets with and without the 0.05 w/o  $\text{TiO}_2$  addition, respectively.

The effect of the  $\text{TiO}_2$  addition is to increase the lattice constant of  $\text{UO}_2$  by 0.094% at  $1200^\circ\text{C}$ . The lattice constant at  $1200^\circ\text{C}$  without the  $\text{TiO}_2$  addition is equal to that at  $1080^\circ\text{C}$  with the 0.05 w/o  $\text{TiO}_2$  addition.

This temperature difference could be well compared with the suppression of sintering temperature by  $\text{TiO}_2$  that had been observed previously.

It is believed that the increase in lattice expansion due to the  $\text{TiO}_2$  addition would give rise to the activated sintering of  $\text{UO}_2$  by the lattice-expansion-induced-enhancement of self diffusion.

### 요 약

고온 X-선 회절방법으로 0.05 w/o  $\text{TiO}_2$  첨가로 인한  $\text{UO}_2$  활성화 소결기구에 미치는 영향을 조사하였다.

$1200^\circ\text{C}$ 에서  $\text{TiO}_2$ 를 첨가한  $\text{UO}_2$ 와 첨가하지 않은  $\text{UO}_2$  격자상수의 열팽창은 상온에서의 격자상수 보다 각각 1.448%와 1.354% 더 컸으며  $\text{TiO}_2$ 를 첨가한 경우가 약 0.094% 더 컸었다. 또한 0.05 w/o  $\text{TiO}_2$ 를 첨가한  $\text{UO}_2$  pellet의  $1080^\circ\text{C}$ 에서의 격자상수는  $1200^\circ\text{C}$ 에서의  $\text{UO}_2$  격자상수와 동일하였다.

이 온도차이는  $\text{UO}_2$  소결시 0.05 w/o  $\text{TiO}_2$ 의 첨가로 인하여 강하된 소결온도와 잘 일치된다.

이와같이  $\text{TiO}_2$ 의 미량첨가가 고온에서  $\text{UO}_2$  격자상수의 열팽창을 증가시켜  $\text{UO}_2$ 의 확산을 촉진시킴으로서 활성화 소결에 영향을 준다고 생각된다.

## 1. Introduction

Several investigations<sup>1-9)</sup> have been previously made on the effect of additions of various metallic oxides for sintering characteristics of  $\text{UO}_2$ . Among these,  $\text{TiO}_2$  is known to be the most effective additive. The optimum  $\text{TiO}_2$  addition for the activated sintering of  $\text{UO}_2$  pellet was reported to be in the neighbourhood of 0.05 w/o.

By the addition of 0.05 w/o  $\text{TiO}_2$ , the sintering temperature of  $\text{UO}_2$  pellet to obtain the high density pellet could be lowered as much as  $170^\circ\text{C}$ <sup>9)</sup>.

There are several explanations for the mechanism of activated sintering of  $\text{UO}_2$  by  $\text{TiO}_2$  addition.

The activated sintering had been explained by the enhancement of  $\text{UO}_2$  self diffusion rate due to the presence of a local liquid phase at grain boundaries because of the  $\text{TiO}_2$  addition at sintering temperature. However, Arthur and Scott showed that the  $\text{UO}_2$ - $\text{TiO}_2$  system is a simple eutectic system and its eutectic temperature is  $1645^\circ\text{C}$ <sup>1)</sup>. The greatest effect of  $\text{TiO}_2$  on  $\text{UO}_2$  sintering is at about  $1400^\circ\text{C}$ , however, where no liquid phase is present.

Hj. Matzke<sup>3)</sup> suggested that small amounts of  $\text{TiO}_2$  are soluble in  $\text{UO}_2$  at elevated temperatures and a fraction of the Ti ion probably occupy interstitial positions as positive ions.

Watson and Welder<sup>4)</sup> considered that  $\text{TiO}_2$  acts as a high temperature oxidizing agent with some possible solution of Ti ions in the surface layers of the  $\text{UO}_2$  particles.

Thus, the activated sintering of  $\text{UO}_2$  with  $\text{TiO}_2$  addition is probably due to the increase in uranium bulk diffusion rate via interstitial solution of titanium.

None of the above explanations appears to give a satisfactory answer for the effect of  $\text{TiO}_2$  addition on  $\text{UO}_2$  sintering.

The present study was undertaken to inves-

tigate the effect of  $\text{TiO}_2$  addition on the thermal expansion of  $\text{UO}_2$  lattice constant during sintering of  $\text{UO}_2$  in order to clarify the mechanism of activated sintering.

## 2. Experiment

### 1) Sample Preparation

As received depleted  $\text{UO}_{2+x}$  powder was reduced in hydrogen atmosphere at  $850^\circ\text{C}$  for 24 hours to obtain a near-stoichiometric compound usually of  $\text{UO}_{2.02}$ <sup>9)</sup>.  $\text{UO}_2$  powder with 0.05 w/o  $\text{TiO}_2$  addition was mixed, and 1 w/o polyvinyl alcohol was added as a binder. The  $\text{UO}_2$  powders were granulated to approximately 200 mesh size by mechanical mixing and 0.2 w/o of zinc stearate was added as a lubricant. Then, the  $\text{UO}_2$  powders with and without 0.05 w/o  $\text{TiO}_2$  addition were compacted at room temperature applying the compacting pressure of 72 tsi. The green compacts were presintered in hydrogen atmosphere at  $850^\circ\text{C}$  for 24 hours in order to drive off the volatile materials such as the binder and lubricant.

### 2) X-ray Diffraction

X-ray diffraction analyses were made with a recording diffractometer\*, using  $\text{Cu K}\alpha$  radiation, a scanning rate of  $0.5^\circ/\text{min}$  in  $2\theta$  and a chart speed of 2 cm/min providing reproducible readings to the nearest  $0.02^\circ$  for  $2\theta$ . The specimen was heated in a heating unit\*\* whose heating element is tungsten wire. The temperature was measured with Pt-10% Rh thermocouple. The arrangement for diffraction angle measurements is as shown in Fig. 1.

Diffraction angles for the (311), (222), (331), (420) and (422) planes of the  $\text{UO}_2$  pellet were measured at room temperature,  $200^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $600^\circ\text{C}$ ,  $800^\circ\text{C}$ ,  $900^\circ\text{C}$ ,  $1000^\circ\text{C}$ ,

\* Shimadzu Automatic Recording X-Ray Diffractometer, Type VD-1

\*\* Shimadzu Specimen Heating Unit in Use for X-ray Diffractometer Model HX-2

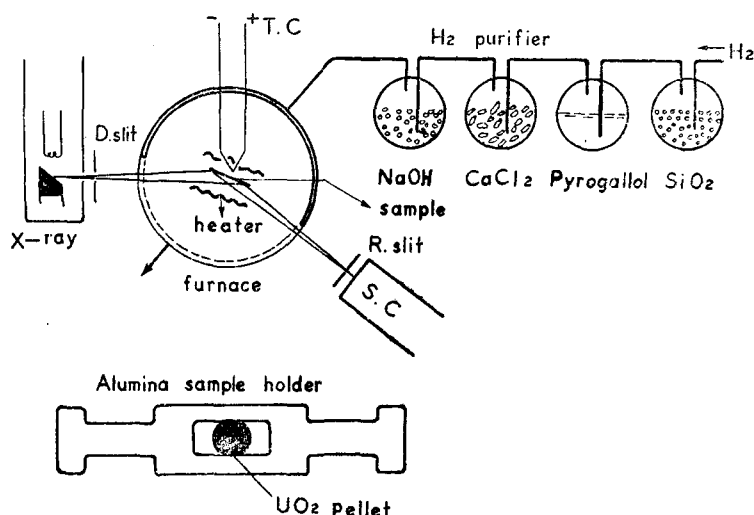


Fig. 1. High temperature X-ray diffractometer

1100°C and 1200°C, respectively in hydrogen atmosphere.

### 3. Results and Discussion

The lattice constants were calculated from

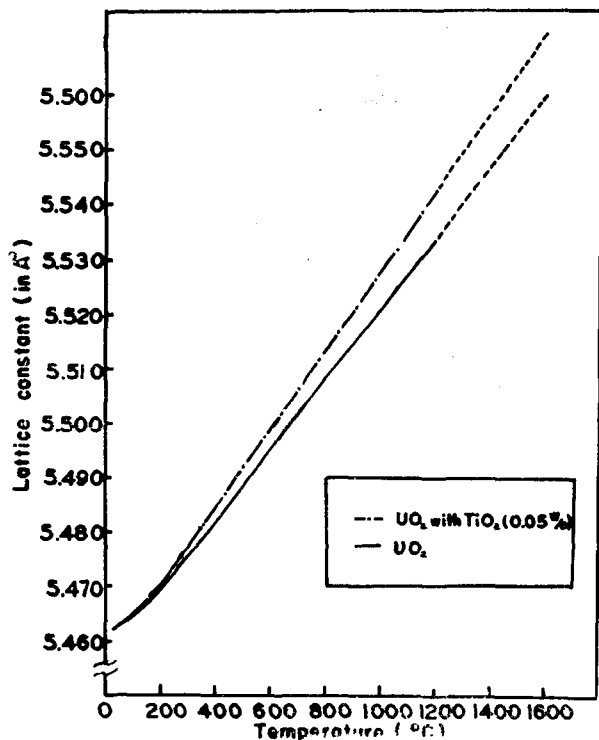


Fig. 2. Variation of lattice constants with temperature

the measurements of "d" values by the Wilson method<sup>11)</sup>. The lattice constants of  $\text{UO}_2$  with and without 0.05 w/o  $\text{TiO}_2$  at different temperatures are given in table I. Lattice parameters of  $\text{UO}_2$  with and without 0.05 w/o  $\text{TiO}_2$  are plotted as a function of temperature in Fig. 2.

It shows that the lattice constant increases linearly with increasing temperature above

Table 1. Lattice constant (in Å unit) at different temperatures of  $\text{UO}_2$  with and without  $\text{TiO}_2$  addition

Sample Temp. °C	$\text{UO}_2$	$\text{UO}_2 + 0.05 \text{ w/o } \text{TiO}_2$
Room temp.	5.463	5.463
200	5.469	5.470
400	5.483	5.485
600	5.497	5.500
800	5.507	5.512
900	5.515	5.521
1000	5.523	5.528
1100	5.529	5.535
1200	5.537	5.543

200°C, and the lattice constant at 1200°C without the  $\text{TiO}_2$  addition is equal to that at 1080°C with the  $\text{TiO}_2$  addition.

If the lattice constant varies linearly with increasing temperature above 1200°C, which is shown as dotted lines in Fig. 2, the lattice constant at 1600°C of  $\text{UO}_2$  without the  $\text{TiO}_2$  addition is equal to that of  $\text{UO}_2$  with  $\text{TiO}_2$  addition at the neighbourhood of 1400°C.

This temperature difference could be well

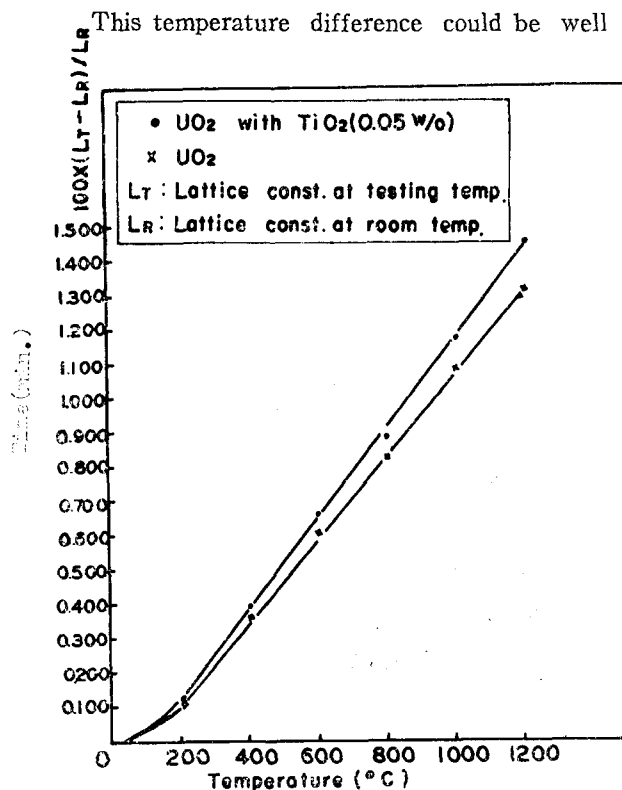


Fig. 3. Lattice constants relative to value at 25°C

related to the suppression of sintering temperature by the  $\text{TiO}_2$  addition that was obtained from a previous experiment<sup>8)</sup>.

Lattice constants relative to that of room temperature are plotted in Fig. 3.

At 1200°C, the thermal expansion of the  $\text{UO}_2$  lattice were 1.448% and 1.354% greater when they were compared with that at room temperature for pellets with and without  $\text{TiO}_2$  addition, respectively.

Therefore, the effect of the  $\text{TiO}_2$  addition is

to increase the lattice constant by 0.094% at 1200°C.

Since the body centered hole is the largest in  $\text{UO}_2$  lattice as shown in Fig. 4, the positive titanium ions would probably occupy the body centered holes as an interstitial.

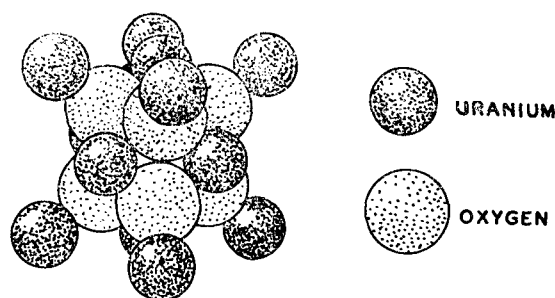


Fig. 4. Structure of  $\text{UO}_2$

This interstitials would cause distortion of the  $\text{UO}_2$  lattice.

These distortion will alter the lattice constant. The change is equivalent to the lattice expansion caused by the defect considered as a center of pressure.

As a result, the enhanced thermal expansion of the  $\text{UO}_2$  lattice due to the  $\text{TiO}_2$  addition would give rise to the enlargement of the body centered hole area of the  $\text{UO}_2$  structure and the decrease in the binding energy between the lattice atoms.

It is believed that the aforementioned effect would enhance self diffusion of  $\text{UO}_2$  and would increase the rate of densification of  $\text{UO}_2$ .

#### 4. Conclusions

As a result of this investigation, the following conclusions can be made.

1) The lattice constants of  $\text{UO}_2$  with and without a  $\text{TiO}_2$  addition increase linearly with increasing temperature above 200°C.

2) The effect of the 0.05w/o  $\text{TiO}_2$  addition is to increase the  $\text{UO}_2$  lattice constant by 0.094% at 1200°C.

3) The lattice constant of  $\text{UO}_2$  without the  $\text{TiO}_2$  addition at 1200°C is equal to that at

1080°C with the 0.05w/o TiO<sub>2</sub> addition. This temperature difference could be well related to the suppression of sintering temperature by the TiO<sub>2</sub> addition.

4) The mechanism of activated sintering of UO<sub>2</sub> by TiO<sub>2</sub> additions can be explained in terms of the UO<sub>2</sub> lattice expansion due to the probable occupancy of Ti ions at the body centered holes of the lattice which would give rise to the enhancement of UO<sub>2</sub> diffusion and, in turn, UO<sub>2</sub> sintering.

#### References

- 1) G. Arthur and D. Scott, Trans. Brit. Cer. Soc., **63**, 417 (1964)
- 2) C. H. Chalder, N. H. F. Bright, D. L. Paterson and L. C. Watson, 2nd UN Conf., Geneva **6**, 620 (1958)
- 3) H. J. Matzke, J. of Nucl. Mat. **20**, 328-331 (1968)
- 4) J. F. Watson and D. R. Willer, Iowa State Report IS-221 (1960)
- 5) B. E. Scaner, Am. Cer. Bull. **38**, 494 (1959)
- 6) K. Suzuki, K. Maruya and T. Kubado, Nippon Gensh Gakku, **5**, 587 (1963)
- 7) H. G. Sowman and G. L. Ploetz, KAPL-1556 (1956)
- 8) B. W. Lee, and K. S. Im, AERI Report, **10**, 837 (1970)
- 9) W. K. Park, and B. W. Lee, AERI Report, **9**, 781 (1969)
- 10) A. B. Auskern and J. Bell, J. Nucl. Mat. **3**, 311-319 (1961)
- 11) H. S. Peiser, X-ray diffraction by poly-crystalline materials, Chapman & Hall Limited, London, 393 (1960)