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PREPARATIONS OF HIGH DENSITY  
(Th, U)O<sub>2</sub> PELLETS

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Preparations of High Density (Th,U)O<sub>2</sub> Pellets

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Preparations of high density and homogeneous (Th,U)O<sub>2</sub> pellets by a powder metallurgy method were examined. (Th,U)O<sub>2</sub> powders were prepared by calcining coprecipitates of ammonium uranate and thorium hydroxide derived from nitrates and mixed sols, and by calcining mixed oxalates precipitated from nitrates. (Th,U)O<sub>2</sub> pellets were characterized with respect to sinterability, lattice parameter, microstructure homogeneity and stoichiometry. Sintering atmospheres had a significant effect upon all the properties of the derived pellets. The sinterability of (Th,U)O<sub>2</sub> was most favourable in oxidizing and reducing atmospheres for ThO<sub>2</sub>-rich and UO<sub>2</sub>-rich compositions, respectively, and can be enhanced by presence of water vapour in sintering atmospheres. In addition, highly homogeneous (Th,U)O<sub>2</sub> pellets with 99 % in theoretical density were derived from the sol powders.

**Keywords :** (Th,U)O<sub>2</sub>, Pellet, Mixed Sol, Sinterability, Sintering Atmosphere, Water Vapour

高密度 (Th, U) O<sub>2</sub> ペレットの製造

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粉末冶金法による高密度かつ均質な (Th, U) O<sub>2</sub> ペレットの製造の検討を行った。(Th, U) O<sub>2</sub> 粉末は、硝酸塩および混合ゾルから得たウラン酸アンモンと水酸化トリウムとの共沈物と、硝酸塩から得た混合シュウ酸塩とを仮焼することにより調製した。(Th, U) O<sub>2</sub> ペレットは焼結性、格子定数、微細構造、均質性および化学量論性についてその特性を調べた。焼結雰囲気は得られたペレットの特性に対して重要な効果をもつことが分った。(Th, U) O<sub>2</sub> の焼結性は、高ThO<sub>2</sub> および高UO<sub>2</sub> 組成で各々酸化性および還元性雰囲気において最も良好であった。さらに、理論密度99%で非常に均質な (Th, U) O<sub>2</sub> ペレットがゾル粉末から得られた。

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## 1. INTRODUCTION

$\text{ThO}_2$  and  $(\text{Th},\text{U})\text{O}_2$  as nuclear fuels are used in the forms of coated fuel particles for high-temperature gas-cooled reactors (HTGR) and pellets for light and heavy water reactors. Efforts for the preparations of  $\text{ThO}_2$  and  $(\text{Th},\text{U})\text{O}_2$  pellet fuels<sup>(1)</sup> have been conducted in  $\text{ThO}_2$  loadings for critical facility and mixed  $\text{ThO}_2$ - $\text{UO}_2$  core loadings for the Shippingport light water breeding reactor (LWBR), Borax IV, Elk River and Indian Point reactors.  $\text{ThO}_2$ -based pellets with theoretical density of below 94 % and  $\text{UO}_2$  concentration of less than 10 wt%, have been generally prepared by usual powder metallurgy procedures (mixing the powders, adding binders and sintering). For the LWBR program, high density  $(\text{Th},\text{U})\text{O}_2$  pellets (greater than 97 %T.D. ) have been required to achieve a greater breeding ratio. However, in many cases, extensive powder milling (> 10 h), large binder additions, high pressure for pellet-forming (> 500 MPa) and severe sintering temperatures (> 2000 K) have been required to prepare high density  $\text{ThO}_2$ -based fuel pellets.

Sintered densities are greatly affected by sintering atmospheres, and it is well known that the presence of water vapour in the atmosphere results in enhancing the sintering rates and lowering the sintering temperature in some oxides

such as  $\text{UO}_2$ <sup>(2)</sup> and  $\text{ThO}_2$ <sup>(3)</sup>. Water vapour has been used for sintering of  $\text{ThO}_2$ -based fuel pellets mainly in order to remove a hydrocarbon, though its effect on sinterability is uncertain. On the other hand, the sol-gel process has a potential for the preparation of high density pellets in a remotely operated facility. The process has been used for the preparation of  $\text{UO}_2$ ,  $\text{ThO}_2$ ,  $\text{PuO}_2$  and these mixed oxide fuel particles for HTGRs and for vibratory compacting into fuel rods in LWRs and HWRs, and has been considered as a conversion step to prepare feed materials for pelletized fuels.  $\text{ThO}_2$  or  $(\text{Th,U})\text{O}_2$  powder has been prepared by drying a sol produced by one of the sol-gel process. The use of the sol-derived powder as a feed material offered advantages of obtaining homogeneous mixture and lowering the sintering temperature. However, the preparation of  $\text{ThO}_2$ -based fuels with high density of above 97 %T.D. and high uranium concentration of above 10 mol% has not been found.

Other approaches to preparation of high density  $\text{ThO}_2$ -based pellets have been carried out by some improved procedures, for example, freeze-dry process<sup>(4)</sup> and microwave denitration method<sup>(5)</sup>. These methods are very attractive because of their capability for producing oxide powders directly from salt solutions.

The present study dealt with some preparation procedures of high density  $(\text{Th,U})\text{O}_2$  pellets on a laboratory scale. The aim of this study was mainly focused on the usefulness of



$\text{ThO}_2\text{-UO}_3$  mixed sols as a starting solution to obtain the pellets with high density and good homogeneity and the effect of water vapour and stoichiometry on sinterability of  $(\text{Th,U})\text{O}_2$  pellets.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Powder preparations

#### 2.1.1 $\text{NH}_4\text{OH}$ coprecipitation

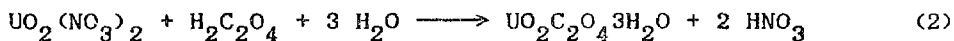
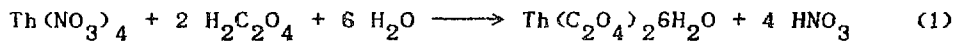
The starting solutions were mixed solutions of thorium and uranyl nitrates with U concentration of 10 ~ 90 mol% and  $\text{ThO}_2\text{-UO}_3$  mixed sols under 7, 20 and 40 mol%  $\text{UO}_3$ , in which the heavy atom concentrations were above about 1 mol/l. About 0.5 mol/l  $\text{NH}_4\text{OH}$  was added slowly under vigorous stirring at ambient temperature. Thorium is precipitated as thorium hydroxide ( $\text{Th}(\text{OH})_4$ ) and uranium as ammonium uranate ( $\text{AU} : \text{UO}_3\text{nNH}_3\text{mH}_2\text{O}$ , where  $\text{n+m}=2$ ). On the other hand, colloid fractions of  $\text{ThO}_2$  and  $\text{UO}_3$  in the mixed sols were about 95 and 50 ~ 30 %, respectively<sup>(6)</sup>. The colloid fraction of  $\text{UO}_3$  in the mixed sols is lower than that of  $\text{ThO}_2$  and decreases with the increase of U concentration. Therefore the instability of  $\text{UO}_3$  colloids in the mixed sol is more prominent at higher U concentration, and  $\text{UO}_3$  shows a trend to precipitate selectively. In this study, the mixed sols not containing precipitates, obtained after sufficient stirring, were used to prevent inhomogeneity of the pellet.

After coprecipitation, the yellow coprecipitate was separated by a centrifugal separation machine, being followed by

washing with a diluted  $\text{NH}_4\text{OH}$  solution and then air-drying. The obtained mass was crushed, pulverized with an agate mortar and pestle, and then was calcined at  $600^\circ\text{C}$  for 1 h in air. The powder calcined was ball milled for 1h under water, before being annealed in  $\text{H}_2$  at  $800^\circ\text{C}$  for 4 h in order to attain to stoichiometry.

### 2.1.2 Oxalate process

The starting solutions were only mixed solutions of thorium and uranyl nitrates. Oxalic acid was added slowly to the solutions with vigorous stirring, which resulted in the precipitation of thorium and uranyl oxalates<sup>(7)</sup>:



Excess water was evaporated at  $150^\circ\text{C}$  in air in order to completely collect  $\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  dissolving in the excess water. The solubility of  $\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  in water has been reported to be about  $0.017 \text{ mol/l}$ <sup>(8)</sup>, which corresponds to about 10% U in a 1 mol/l mixed nitrate solution with 20 mol% U. The obtained mass was pulverized, calcined at  $900^\circ\text{C}$  for 1 h in air and then was dry-milled for 1 h.

### 2.2 Pellet preparations

(Th,U)O<sub>2</sub> powders derived from the NH<sub>4</sub>OH coprecipitation and the oxalate precipitation-evaporation processes<sup>(8)</sup> were pressed into pellets at a pressure of 200 MPa without binders and lubricants. The sinterings were performed at 1500 °C for 10 h or 1750 °C for 3 h (only for the oxalate derived pellets) in several atmospheres, as summarized in Table 1. Heating and cooling rates during sintering were set at 100 K/deg to prevent the pellets from crackings during heating and cooling. Supply of water vapour in a furnace was made by bubbling air or He-4%H<sub>2</sub> in a temperature controlled deionized water. The front and back portions of Al<sub>2</sub>O<sub>3</sub> furnace tube were heated at 200 °C to prevent from condensation of water vapour.

Pellets sintered in oxidizing atmospheres (air or wet air) were furthermore annealed in H<sub>2</sub> at 1000 °C for 24 h in order to be reduced to a stoichiometry.

### 2.3 Characteristics measurements

Bulk densities of sintered pellets were determined from the bulk volumes measured by a mercury pycnometer method<sup>(9)</sup>. The accuracy for measuring volumes was about  $\pm 1 \times 10^{-9} \text{ m}^3$ , which corresponded to about  $\pm 0.1 \%$  in bulk density of ThO<sub>2</sub> with 10 g in weight and 10 Mg/m<sup>3</sup> in density.

X-ray diffraction with a Cu radiation was made on the sintered pellets. In determining the lattice parameter, the

extrapolation method with use of the Nelson and Riley equation was applied to 15 diffraction peaks at  $2\theta > 100^\circ$ .

As-polished surfaces of the sintered pellets were observed by an electron probe microanalyser (EPMA) in order to check the inhomogeneity of composition.

Non-stoichiometries of the pellets sintered in oxidizing atmospheres were estimated by weight analysis. O/M ratio for  $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$  was calculated from the equation :

$$\begin{aligned} \text{O/M} &= 2 + x \\ &= 2 + \frac{M}{16} \frac{\Delta W}{W} \end{aligned} \quad (3)$$

where M is the molecular weight of  $\text{Th}_{1-y}\text{U}_y\text{O}_{2.00}$ , W the sample weight at  $\text{O/M} = 2.00$  and  $\Delta W$  the weight change relative to the W.

### 3. RESULTS

#### 3.1 $\text{NH}_4\text{OH}$ coprecipitate-derived pellets

##### 3.1.1 Densities

Green densities of pellets pressed from two kinds of coprecipitated powders are shown in Fig. 1. It is found that the green densities were nearly constant up to 40 mol%  $\text{UO}_2$ , and that those of pellets pressed from the mixed nitrate solution coprecipitated powders were larger than those of the mixed sol-derived pellets. In general, the compressibility of powder is closely related to its characteristics, in particular, surface area and morphology. The surface area would have an inverse relationship to the compressibility, because the compressibility for powders with smaller particle size is lower and the particle size have an inverse relationship to the surface area. Therefore, the particle size for the mixed sol-derived powders would be small, compared with the mixed nitrate solution coprecipitated powders. The green density decreased rapidly with  $\text{UO}_2$  concentration from 40 to 70 mol%  $\text{UO}_2$  and then saturated at almost 35 %T.D. above 70 mol%  $\text{UO}_2$ . This suggests that the particle size of the  $\text{UO}_2$  powder is much smaller than that of the hydroxide-derived  $\text{ThO}_2$  powder.

Fig. 2 shows the bulk densities of sintered pellets derived

from the coprecipitated powders as a function of their composition. It is clear that the densities of pellets obtained for the mixed sol-derived powders are higher than those for the mixed nitrate solution-derived powders. The sol-derived pellets sintered at 1500 °C in wet air attained the densities of about 99 %T.D.. This result indicates that the mixed sol-derived powders should have higher sinterability than the mixed nitrate solution derived ones.

Sintering atmospheres have significant effects upon the sinterability of (Th,U)O<sub>2</sub>. The sintering can be most enhanced in oxidizing atmospheres up to 50 mol% UO<sub>2</sub>. On the other hand, the sintering in reducing atmospheres would be more effective above 50 mol% UO<sub>2</sub>. Effects of water vapour on the sinterability are recognizable in both oxidizing and reducing atmospheres for the sol-derived pellets. Consequently, the sinterability of (Th,U)O<sub>2</sub> can be enhanced by the presence of water vapour in sintering atmospheres.

As shown in fig.2, the composition dependence of the sinterability for the powders from the mixed nitrate solutions indicates that the density appears to take minimum values at a composition of 50 ~ 60 mol% UO<sub>2</sub>. The result demonstrates that the sinterability for (Th,U)O<sub>2</sub> powders would decrease with the increase of concentration of the second component.

### 3.1.2 Xray diffractions

Fig. 3 shows the composition dependence of the lattice parameters obtained for the pellets which were sintered in wet He-4%H<sub>2</sub> and nearly stoichiometric. UO<sub>2</sub> and ThO<sub>2</sub> have the CaF<sub>2</sub> type face-centered cubic structures. The lattice parameters of ThO<sub>2</sub> and stoichiometric UO<sub>2</sub> determined in this study were  $0.55971 \pm 0.00003$  and  $0.54699 \pm 0.00003$  nm, respectively. The present data were subjected to the Vegard's law for all compositions, which suggests that all pellets show complete solid solutions.

Fig. 4 shows half widths of (600) and (440) diffraction peaks as a function of composition. The line broadening appears to take maximum values at a composition of 50 ~ 60 mol% UO<sub>2</sub>. The dependence of the line broadening on composition which is very similar to that of the bulk density indicates that there would be close relationship between the bulk density and the line broadening. This is reasonable because the line broadening is very closely related to the size of crystal grain, lattice strain and inhomogeneity of composition.

### 3.1.3 Non-stoichiometry

Fig. 5 shows the O/M ratios of as-sintered pellets in wet air as a function of composition. The O/M ratio increases linearly up to 40 mol% UO<sub>2</sub> with UO<sub>2</sub> concentration and shows a rapid increase at about 50 mol% UO<sub>2</sub>. It increases only slightly above 50 mol% UO<sub>2</sub>. The O/M ratio at 50 mol% UO<sub>2</sub> was about 2.25,



which corresponds to +5 of uranium mean valence. In general,  $\text{ThO}_2\text{-UO}_2$  solid solutions with  $\text{UO}_2$  concentration up to about 40 mol% are stable in atmospheres with high oxygen potentials, as mentioned in chap. 4.

#### 3.1.4 Microstructure observations

Fig. 6 shows ceramographs and U-M $\beta$  X-ray images of the mixed col-derived pellets which were sintered in wet atmospheres. The pellets sintered in wet air show very smooth polished surfaces, that is, have low porosities. The size of pores appears to be almost below about 2  $\mu\text{m}$ . On the other hand, those of the pellets sintered in wet  $\text{He-4\%H}_2$  show higher porosities. The fraction of small pores with diameter of about 1  $\mu\text{m}$  would be high compared with the pellets sintered in wet air. Homogeneity of composition in both pellets was very good, as shown in the U-M $\beta$  images.

Fig. 7 shows typical ceramographs and X-ray images, U-M $\beta$  for 40 mol%  $\text{UO}_2$  and Th-M $\alpha$  for 60 and 80 mol%  $\text{UO}_2$ , of the pellets obtained by sintering the powders derived from the mixed nitrate solutions. The observations indicate that the porosities are highest for both 60 mol%  $\text{UO}_2$  pellets and the pore size are very large (above  $\sim 10 \mu\text{m}$ ). The worst of the inhomogeneity is observed for 60 mol%  $\text{UO}_2$  pellets sintered in wet  $\text{He-4\%H}_2$ , and on the other hand, the pellets sintered in wet air show good homogeneity. The fact that high porosities and

worse homogeneities are obtained for about 60 mol%  $\text{UO}_2$  agrees with those for the composition dependences of the bulk density and the line broadening.

Sol-derived powders of  $(\text{Th,U})\text{O}_2$  has been prepared mainly by drying and milling  $\text{ThO}_2\text{-UO}_3$  sols. The high sinterability of the sol-derived powder indicates that the powder would be very active or have large surface area. In the present study, sol-derived powders were prepared by  $\text{NH}_4\text{OH}$  coprecipitating from  $\text{ThO}_2\text{-UO}_3$  mixed sols, followed by wet milling and calcining. It was found that the sinterability for the sol-derived powders was clearly higher than for the powder derived from the mixed nitrate solutions. Fig. 8 shows secondary electron images of two kinds of  $\text{Th}_{0.9}\text{U}_{0.1}\text{O}_2$  powders derived from  $\text{NH}_4\text{OH}$  coprecipitates. The powders were annealed at  $800^\circ\text{C}$  in  $\text{H}_2$  after wet milling. The particle size of the sol-derived powder is apparently smaller than that of the powder from the other. Moreover, the sol-derived powder is composed of two powders with particle sizes of below about  $1\ \mu\text{m}$  and  $3 \sim 4\ \mu\text{m}$ . Consequently, the high sinterability for the sol-derived powders would be attributed to these characteristics.

### 3.1.5 Annealing at higher temperature after sintering

During sintering or annealing  $(\text{Th,U})\text{O}_2$  pellets at high temperature, selective evaporation of uranium from the surface of  $(\text{Th,U})\text{O}_2$  is an important problem, since vapour pressures of

uranium species over  $(\text{Th,U})\text{O}_2$  are higher than of thorium species. In particular, high temperature annealing in vacuum<sup>(10)</sup> or oxidizing atmosphere<sup>(11)</sup> causes remarkable decrease of uranium concentration near the surface, because vapor pressure of  $\text{UO}_2$  is relatively high and diffusibility of uranium ions in  $(\text{Th,U})\text{O}_{2+x}$  lattice is higher than in stoichiometric  $(\text{Th,U})\text{O}_2$ . It has been reported that the region which are observed in  $(\text{Th,U})\text{O}_2$  reaches to above several tens  $\mu\text{m}$  from the surface in vacuum or oxidizing atmosphere. The  $(\text{Th,U})\text{O}_2$  pellets with theoretical density of about 95 % were used. However, the selective evaporation of uranium from  $(\text{Th,U})\text{O}_2$  may be affected also by the microstructure, such as density, pore and grain structures. It is expected that the selective evaporation in high-density  $(\text{Th,U})\text{O}_2$  pellets would be low in amount, because rapid transport of uranium caused by internal evaporation in pores is probably neglected. Fig. 9 shows a ceramograph at near surface of  $\text{Th}_{0.6}\text{U}_{0.4}\text{O}_2$  pellet prepared from the sol annealed at 1650 °C in He-4% $\text{H}_2$  for 15 h. The decrease of uranium concentration at near surface was not observed.

### 3.2 Oxalate-derived pellets

The preparation of pellets with use of the oxalate-derived powder as a raw powder were carried out only for pure  $\text{ThO}_2$  and  $\text{Th}_{0.8}\text{U}_{0.2}\text{O}_2$ . The sintered densities are summarized in Table 2.

In  $\text{ThO}_2$ , the sintered density can be clearly enhanced by water vapour. On the other hand, the sintered density of the 20 mol%  $\text{UO}_2$  pellet is lower than that of the  $\text{ThO}_2$  pellet, which indicates that the preparation of high-density  $(\text{Th},\text{U})\text{O}_2$  pellets by the oxalate process would be very difficult and would need sintering at higher temperatures. For sintering at  $1750^\circ\text{C}$ , the sintered density in  $\text{He-4\%H}_2$  is higher than in  $\text{Ar-4\%H}_2$ . This result suggests that sinterability in gases with smaller atomic radius would be higher. The increase of sinterability might be attributed to easiness of degas from pores.

The homogeneity of composition for 20 mol%  $\text{UO}_2$  pellets was examined by EPMA observations. Fig.10 shows the as-polished surface and the U-M $\beta$  image. Fig.11 shows the X-ray line scanning patterns. These figures show that there are many spots of uranium, which suggests that a considerable sum of uranyl oxalate may be dissolved in excess water during precipitation and the particle size of the ignited oxalate may be very large. The uranium spots were observed even after annealing at  $1500^\circ\text{C}$  for 100 h in  $\text{He-4\%H}_2$ . Consequently, the prereducing of uranium in the mixed nitrate solution with a reducing agent such as sodium formaldehyde sulfoxylate<sup>(12)</sup>, is necessary to obtain the  $(\text{Th},\text{U})\text{O}_2$  pellets with good homogeneity.

## 4. DISCUSSION

The bulk densities of the mixed sol-derived  $(\text{Th,U})\text{O}_2$  pellets sintered in wet air attained to about 99 %T.D., as shown in fig.2. Their high density should be attributed to the high sinterability of the sol-derived powder whose particles have small sizes and are composed of small and large ones with sizes of below about 1 and 3 ~ 4  $\mu\text{m}$ , respectively. Spaces existing between the large particles would be filled up by the small ones. Consequently, high density pellets with small pores can be prepared by sintering at relatively low temperature. It is obvious that use of sol-derived powders as a raw material is suitable to prepare  $(\text{Th,U})\text{O}_2$  pellets with high density and good homogeneity. However, the preparation of  $(\text{Th,U})\text{O}_2$  pellets with high uranium concentrations from the sol-derived powder may not be recommended, because  $\text{ThO}_2\text{-UO}_3$  mixed sols with high uranium concentration ( above about 40 mol% ) is very unstable so that much  $\text{UO}_3$  precipitate<sup>(6)</sup>, as mentioned in chap 2.1.1.

Sintering in wet atmosphere appears to be very suitable for preparation of  $(\text{Th,U})\text{O}_2$  pellets with high density and good homogeneity. The sinterability can be clearly enhanced by the presence of water vapour in sintering atmospheres. Similar enhancement of sinterability has been observed by Staurt et

al<sup>(2)</sup> for UO<sub>2</sub> pellets sintered in H<sub>2</sub>-N<sub>2</sub>-H<sub>2</sub>O at 1300 °C. They have reported that the sintered density increases with the increase of ratio P(H<sub>2</sub>O)/P(H<sub>2</sub>). The ratio is related to oxygen potential ΔG(O<sub>2</sub>) by

$$\Delta G(O_2) = 2 RT \ln \left( \frac{P(H_2O)}{P(H_2)} \right) + 2 \Delta G^0, \quad (3)$$

where ΔG<sup>0</sup> is standard free energy. The ratio of 0.007 ~ 0.3 corresponds with the oxygen potential of about -440 ~ -350 kJ/mol. Their result indicates that the sinterability of UO<sub>2</sub> increases with the increase of oxygen potentials of sintering atmospheres. On the other hand, high density ThO<sub>2</sub> microspheres with diameter of about 500 μm as fuel kernels in coated fuel particles for HTGR have been prepared by Yamagishi et al<sup>(3)</sup> using the sol-gel method. The ThO<sub>2</sub> gel spheres were sintered at 1300 °C in wet air contained H<sub>2</sub>O of 0.4 ~ 100 %. They have found that the sintered density increased with the increase of the partial pressure of H<sub>2</sub>O or the oxygen potential. The oxygen potentials of the wet atmospheres are in the range of -161 and -113 kJ/mol.

We think that the enhancement of the sintering induced by water vapour would be due to surface effects, in particular, non-stoichiometry at near surface of powders induced by water vapour, although the exact mechanism has not been clear. Any oxygen potential within the range of -440 ~ -350 kJ/mol would be satisfactory for maintaining stoichiometric UO<sub>2</sub>. However, it is

expected that the near-surface would be in non-stoichiometric by strong oxidizing effect of water vapour. Diffusibility of uranium ions in  $\text{UO}_2$  is affected significantly by the non-stoichiometry. For hyper-stoichiometric  $\text{UO}_{2+x}$ , the increase in oxygen interstitial concentration gives the rising of cation diffusion coefficient. Consequently, the sinterability of  $\text{UO}_2$  powder can be enhanced by water vapour, because the near-surface of the powder would be in hyper-stoichiometric. On the other hand,  $\text{ThO}_2$  is very stable compound and  $\text{ThO}_{2+x}$  can not exist in bulk. However, the near-surface could be in slightly hyper-stoichiometric by the presence of water vapour.

Lee and Alcock<sup>(13)</sup> have measured the diffusion of uranium and thorium in  $\text{ThO}_2\text{-UO}_2$  solid solution at 1400 °C in the ranges of stoichiometry of 2.01 to 2.19 for 50 and 25 mol%  $\text{ThO}_2$ . They have observed the increase in the diffusion coefficient with the increase of oxygen stoichiometry, and have concluded that the increase is due to the formation of a  $\text{U}^{+5}\text{-O}_i\text{-U}^{+5}$  defect complex. Consequently, it is expected that the sintering of  $(\text{Th,U})\text{O}_2$  pellets would be affected by the non-stoichiometrics, in the same manner as the sintering of  $\text{UO}_2$  pellets.

Tentative phase diagram of Th-U-O system between 1250 and 1550 °C is shown in Fig. 12<sup>(14)(15)</sup>. The main features of the diagram can be summarized as followed:

1.  $\text{MO}_{2+x}$  phase ( face-centered cubic ) is very stable in the  $\text{ThO}_2$ -rich region of above about 60 mol%  $\text{ThO}_2$ .

2. The  $\text{MO}_{2+x}$  phase is in equilibrium with  $\text{U}_3\text{O}_8$  phase ( orthorhombic ) in the  $\text{UO}_2$ -rich ( above 50 mol%  $\text{UO}_2$  ) and high O/M ( above 2.25 ) region.

As shown in fig. 5, the O/M ratio of  $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$  pellets in the  $\text{UO}_2$ -rich region ( above 50 mol%  $\text{UO}_2$  ) exceeds the permitted value, under which the  $\text{MO}_{2+x}$  phase is stable. Therefore the  $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$  pellets would be composed of  $(\text{Th,U})\text{O}_2$  and  $\text{U}_3\text{O}_8$  phases. Fig. 13 shows mean valences of uranium  $V_u$ , calculated from the O/M ratios, by using the relation<sup>(16)</sup>

$$V_u = 4 + 2x/y. \quad (4)$$

The mean valence has a maximum at about 50 mol%  $\text{UO}_2$ . On the other hand, the inhomogeneity of composition would be prominent at a composition of about 50 mol%  $\text{UO}_2$ , which supports the observation of the microstructure and the result that the line broadening of X-ray peak has a maximum at 50 ~ 60 mol%  $\text{UO}_2$ , as shown in fig. 4. There would be a exact relation between the mean valence and the sintered density. In deed, the sintered density decreases with the increase of the mean valence. Consequently, oxidizing atmospheres, in which the  $(\text{Th,U})\text{O}_{2+x}$  phase can be stable, can enhance the sinterability, but strong oxidizing ones, in which the  $(\text{Th,U})\text{O}_{2+x}$  and  $\text{U}_3\text{O}_8$  phases are in equilibrium, would cause the sinterability to decrease.



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Table 1 Sintering conditions

Sintering atmosphere	Sintering temperature (°C)	Oxygen potential (kJ/mol)
Air	1500	-25
Air/H <sub>2</sub> O(g, 95°C)	1500	-113
He-4%H <sub>2</sub> /H <sub>2</sub> O(g, 20°C)	1500	-293
He-4%H <sub>2</sub>	1500	-473
	1750	-469

Table 2 Green and sintered densities of oxalate-derived pellets

UO <sub>2</sub> concentration (mol%)	Green density (%T. D.)	Sintered density (%T. D.)			
		1500 °C		1750 °C	
		Air	Air/H <sub>2</sub> O	Ar-4%H <sub>2</sub>	He-4%H <sub>2</sub>
0	57.0	91.2	96.5	--	--
0.5	56.8	94.2	--	--	--
20	50.4	57.8	--	89.2	92.7

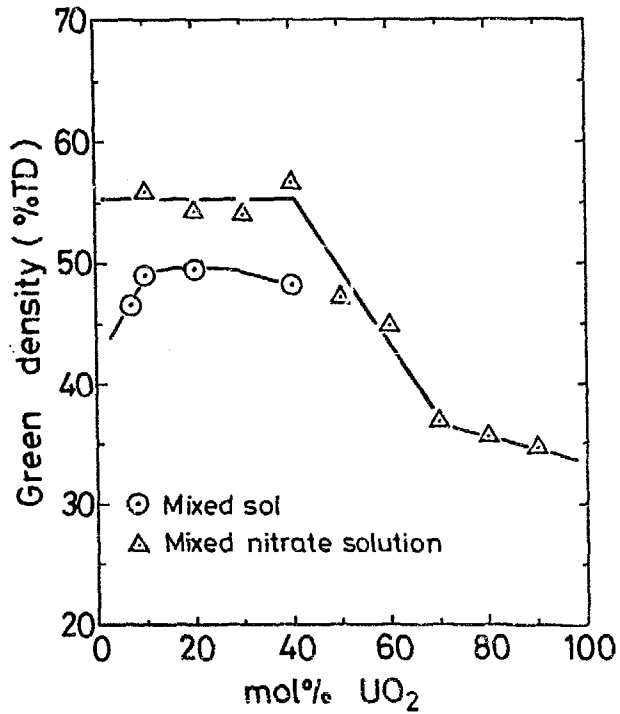


Fig.1 : Green densities of (Th,U)O<sub>2</sub> pellets derived from NH<sub>4</sub>OH coprecipitates

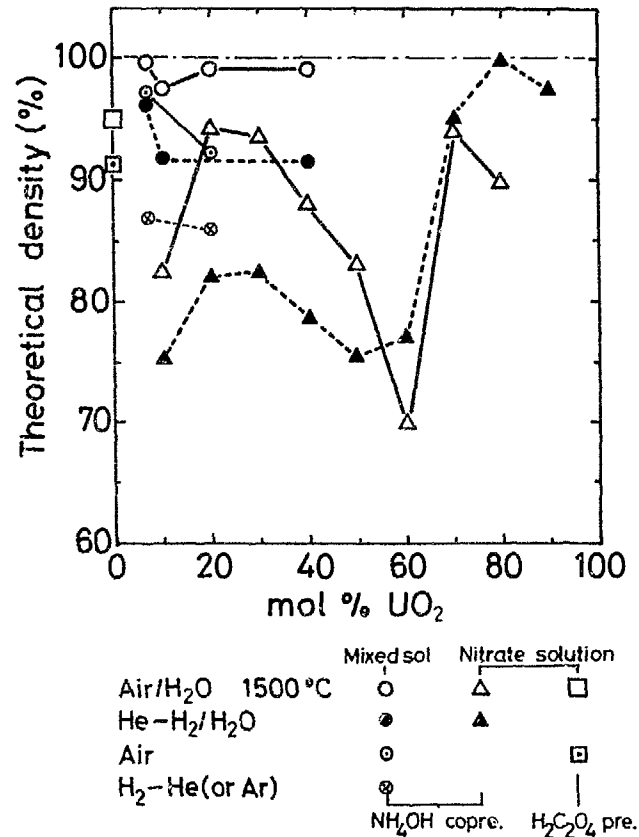


Fig.2 : Sintered density variations on powders, sintering atmospheres and compositions

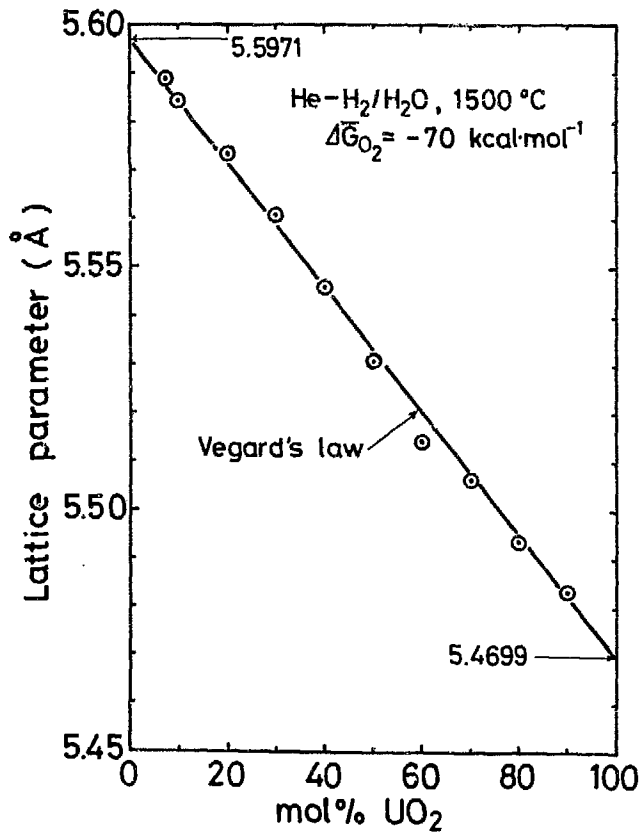


Fig.3 : Lattice parameter-composition curve in near stoichiometric (Th, U)<sub>2</sub>O pellets

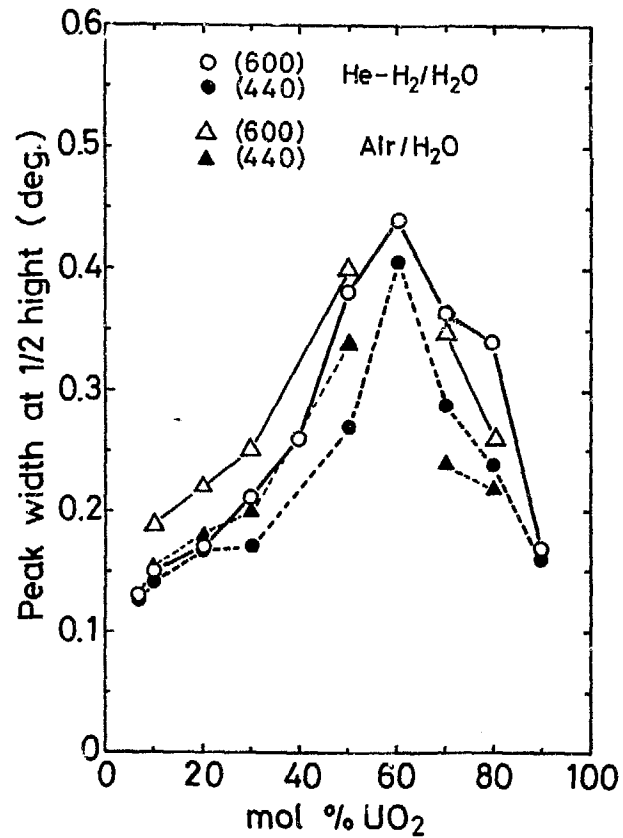


Fig.4 : Composition dependences of half widths of (600) and (440) diffraction peaks in sintered pellets

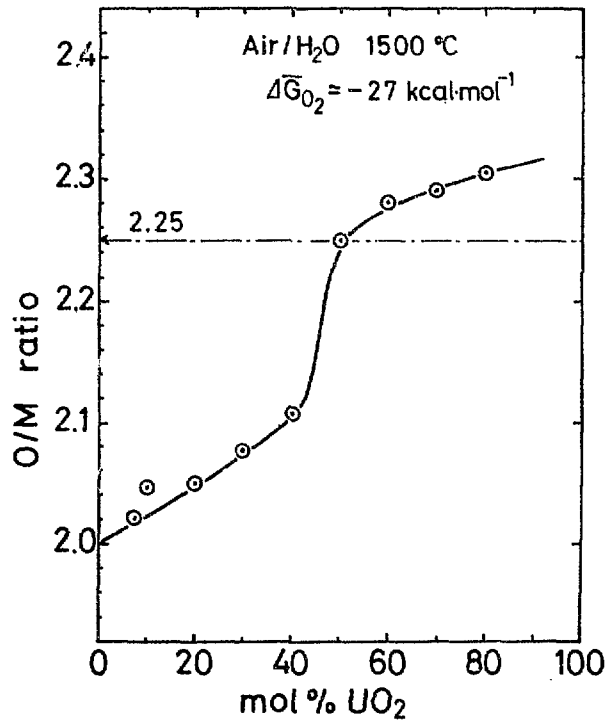
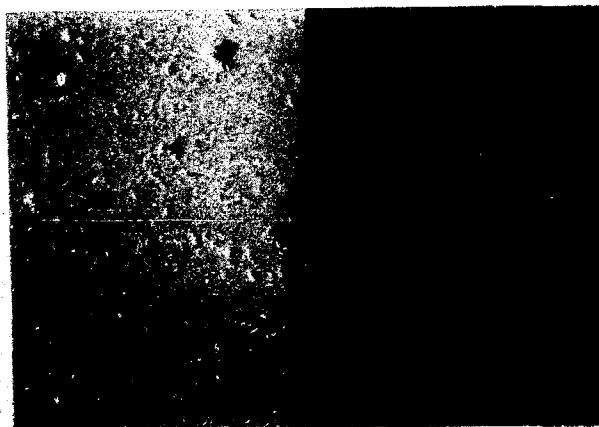
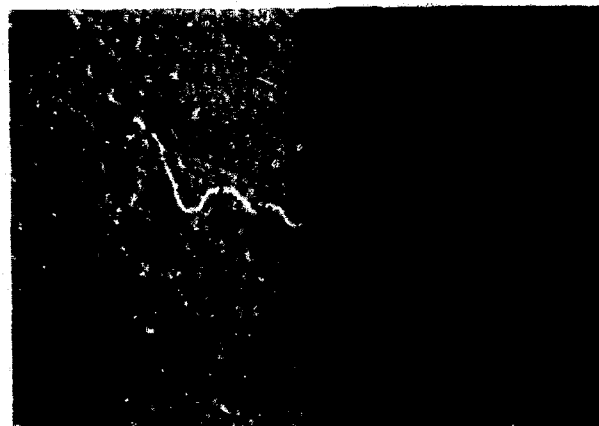


Fig.5 : Composition dependence of O/M ratios in pellets sintered in wet air

7 mol% UO<sub>2</sub> sol



10 mol% UO<sub>2</sub> sol

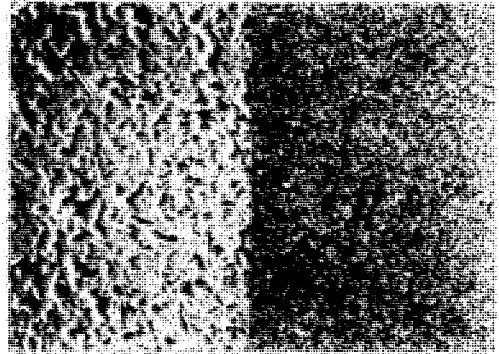
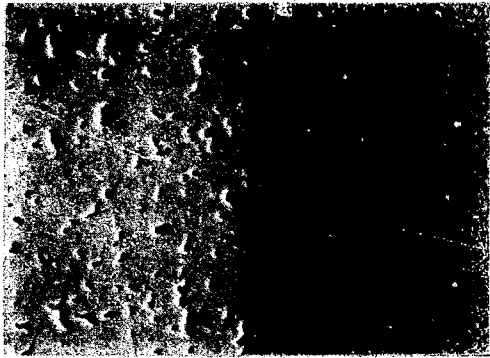


Air/H<sub>2</sub>O 1500 °C

He-H<sub>2</sub>/H<sub>2</sub>O 1500 °C

Fig.6 : Ceramographs and U-Mβ X-ray images of sol-derived pellets sintered in wet atmospheres

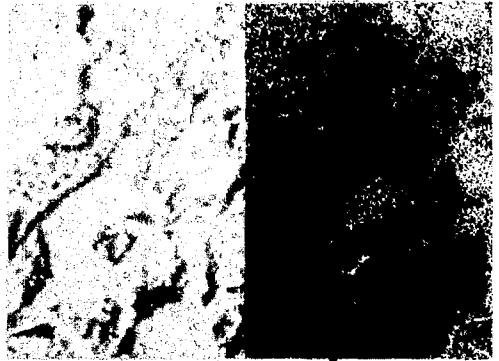
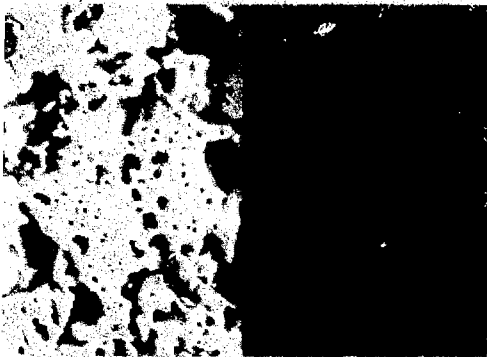
40 mol %



U-M $\beta$

U-M $\beta$

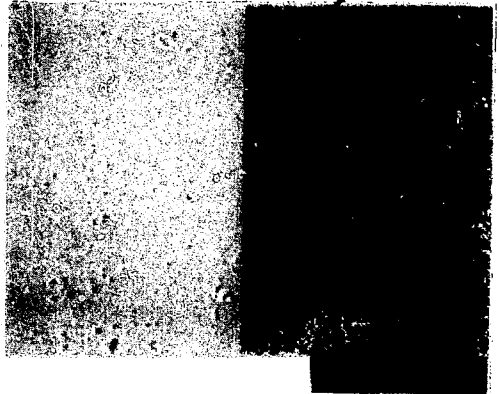
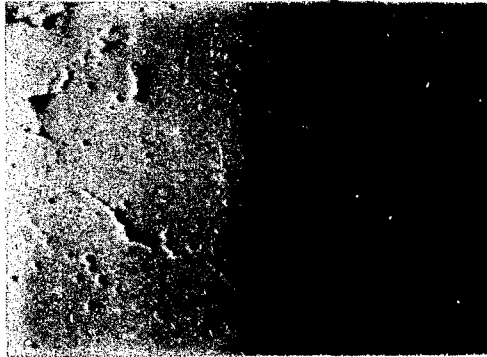
60 mol %



Th-M $\alpha$

80 mol %

Th-M $\alpha$

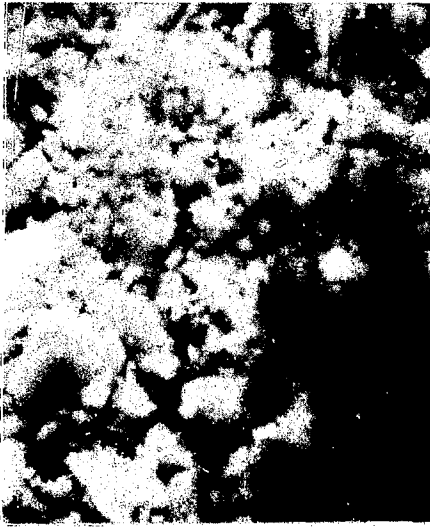


Air/H<sub>2</sub>O 1500 °C

He-H<sub>2</sub>/H<sub>2</sub>O 1500 °C

Fig.7 : Typical ceramographs and X-ray images of nitrate-derived pellets sintered in wet atmospheres





ThO<sub>2</sub>-UO<sub>3</sub> sol-derived



Th(NO<sub>3</sub>)<sub>4</sub>-UO<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub> solution derived  
10 μm

Fig.8 : Secondary electron images of 10 mol% UO<sub>2</sub> coprecipitates derived from the sol and the nitrate

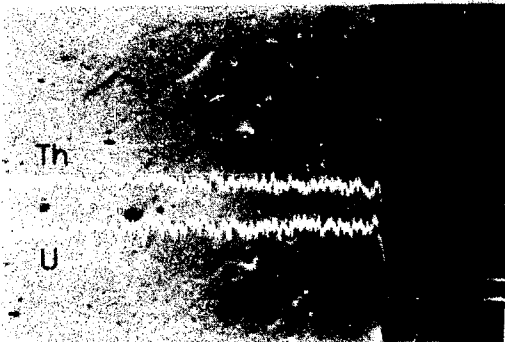


Fig.9 : Ceramograph at the near surface of a Th<sub>0.6</sub>U<sub>0.4</sub>O<sub>2</sub> pellet derived from the sol and annealed at 1650 °C in He-4%H<sub>2</sub> for 15h.



Fig.10 : U-Mβ X-ray images of a oxalate-derived Th<sub>0.8</sub>U<sub>0.2</sub>O<sub>2</sub> pellet

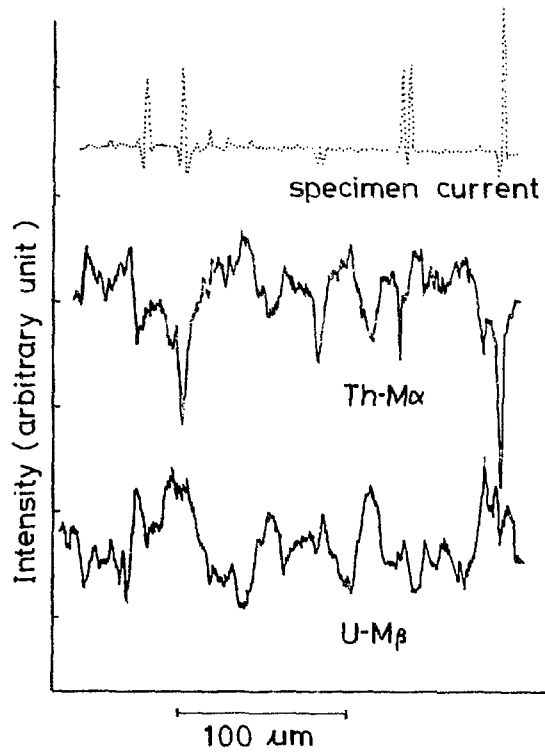


Fig.11 : X-ray line scanings of the oxalate-derived pellet

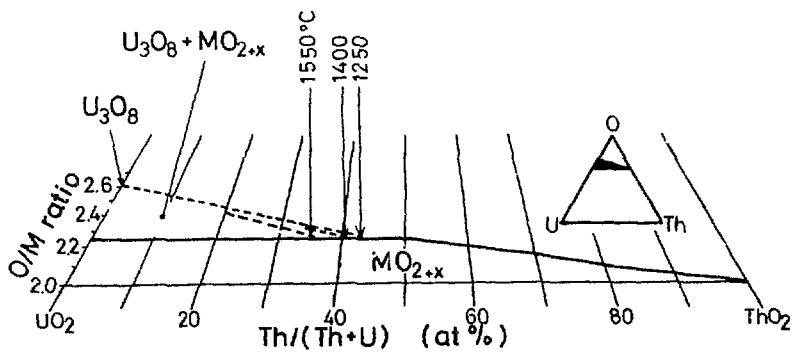


Fig.12 : Tentative phase diagram of Th-U-O system between 1250 and 1550 °C

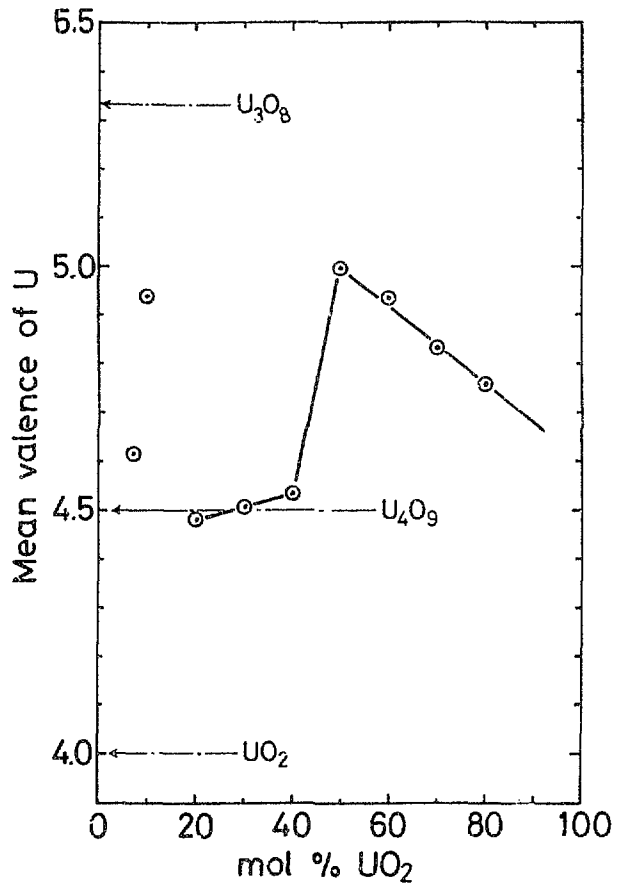


Fig.13 : Composition dependence of mean uranium valences in pellets sintered in wet air