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Preparations of High Density $(Th,U)O_2$ Pellets

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Preparations of high density and homogeneous $(Th,U)O_2$ pellets by a powder metallurgy method were examined. $(Th,U)O_2$ 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. $(Th,U)O_2$ 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 $(Th,U)O_2$ was most favourable in oxidizing and reducing atmospheres for ThO_2-rich and UO_2-rich compositions, respectively, and can be enhanced by presence of water vapour in sintering atmospheres. In addition, highly homogeneous $(Th,U)O_2$ pellets with 99 % in theoretical density were derived from the sol powders.

Keywords : $(Th,U)O_2$, Pellet, Mixed Sol, Sinterability, Sintering Atmosphere, Water Vapour

高密度（Th，U）O_2 ペレットの製造

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赤堀光雄・井川勝市

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粉末冶金法による高密度かつ均質な（Th，U）O_2 ペレットの製造の検討を行った。（Th，U）O_2 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_2 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_2 の焼結性は、高ThO_2 および高UO_2 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_2 ペレットがゾル粉末から得られた。

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1. INTRODUCTION

ThO_2 and $(Th,U)O_2$ 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 ThO_2 and $(Th,U)O_2$ pellet fuels[1] have been conducted in ThO_2 loadings for critical facility and mixed ThO_2-UO_2 core loadings for the Shippingport light water breeding reactor (LWBR), Borax IV, Elk River and Indian Point reactors. ThO_2-based pellets with theoretical density of below 94 % and 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 $(Th,U)O_2$ 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 ThO_2based 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 UO_2[2] and ThO_2[3]. Water vapour has been used for sintering of 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 UO_2, ThO_2, 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. ThO_2 or $(Th,U)O_2$ 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 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 ThO_2-based pellets have been carried out by some improved procedures, for example, freeze-dry process[4] and microwave denitration method[5]. These methods are very attractive because of their capability for producing oxide powders directly from salt solutions.

The present study dealed with some preparation procedures of high density $(Th,U)O_2$ pellets on a laboratory scale. The aim of this study was mainly forcused on the usefulness of

ThO_2-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 $(Th,U)O_2$ pellets.

2. EXPERIMENTAL PROCEDURE

2.1 Powder preparations

2.1.1 NH_4OH coprecipitation

The starting solutions were mixed solutions of thorium and uranyl nitrates with U concentration of 10 ~ 90 mol% and ThO_2-UO_3 mixed sols under 7, 20 and 40 mol% UO_3, in which the heavy atom concentrations were above about 1 mol/l. About 0.5 mol/l NH_4OH was added slowly under vigorous stirring at ambient temperature. Thorium is precipitated as thorium hydroxide ($Th(OH)_4$) and uranium as ammonium uranate (AU : $UO_3nNH_3mH_2O$, where n+m=2). On the other hand, colloid fractions of ThO_2 and UO_3 in the mixed sols were about 95 and 50 ~ 30 %, respectively[6]. The colloid fraction of UO_3 in the mixed sols is lower than that of ThO_2 and decreases with the increase of U concentration. Therefore the instability of UO_3 colloids in the mixed sol is more prominent at higher U concentration, and 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 NH_4OH solution and then air-drying. The obtained mass was crushed, pulverized with an agate mortar and pestle, and then was calcined at 600 °C for 1 h in air. The powder calcined was ball milled for 1h under water, before being annealed in H_2 at 800 °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[7]:

$$Th(NO_3)_4 + 2\ H_2C_2O_4 + 6\ H_2O \longrightarrow Th(C_2O_4)_2 6H_2O + 4\ HNO_3 \quad (1)$$

$$UO_2(NO_3)_2 + H_2C_2O_4 + 3\ H_2O \longrightarrow UO_2C_2O_4 3H_2O + 2\ HNO_3 \quad (2)$$

Excess water was evaporated at 150 °C in air in order to completely collect $UO_2C_2O_4 3H_2O$ dissolving in the excess water. The solubility of $UO_2C_2O_4 3H_2O$ in water has been reported to be about 0.017 mol/l[8], 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 °C for 1 h in air and then was dry-milled for 1 h.

2.2 Pellet preparations

$(Th,U)O_2$ powders derived from the NH_4OH coprecipitation and the oxalate precipitation-evapolation processes[8] 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 $He-4\%H_2$ in a temperature controled deionized water. The front and back portions of Al_2O_3 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_2 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[9]. The accuracy for measuring volumes was about $\pm 1 \times 10^{-9}$ m^3, which corresponded to about ± 0.1 % in bulk density of ThO_2 with 10 g in weight and 10 Mg/m^3 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 $Th_{1-y}U_yO_{2+x}$ was calculated from the equation :

$$O/M = 2 + x$$

$$= 2 + \frac{M}{16}\frac{\Delta W}{W} \qquad (3)$$

where M is the molecular weight of $Th_{1-y}U_yO_{2.00}$, W the sample weight at O/M = 2.00 and ΔW the weight change relative to the W.

3. RESULTS

3.1 NH_4OH 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% 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 UO_2 concentration from 40 to 70 mol% UO_2 and then saturated at almost 35 %T.D. above 70 mol% UO_2. This suggests that the particle size of the UO_2 powder is much smaller than that of the hydroxide-derived 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 ^{o}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_2. The sintering can be most enhanced in oxidizing atmospheres up to 50 mol% UO_2. On the other hand, the sintering in reducing atmospheres would be more effective above 50 mol% UO_2. 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_2 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_2. The result demonstrates that the sinterability for (Th,U)O_2 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_2 and nearly stoichiometric. UO_2 and ThO_2 have the CaF_2 type face-centered cubic structure. The lattice parameters of ThO_2 and stoichiometric UO_2 determined in this study were 0.55971 ± 0.00003 and 0.54699 ± 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_2. 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_2 with UO_2 concentration and shows a rapid increase at about 50 mol% UO_2. It increases only slightly above 50 mol% UO_2. The O/M ratio at 50 mol% UO_2 was about 2.25,

which corresponds to +5 of uranium mean valence. In general, ThO_2-UO_2 solid solutions with 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-Mβ X-ray images of the mixed sol-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 μm. On the other hand, those of the pellets sintered in wet He-4%H_2 show higher porosities. The fraction of small pores with diameter of about 1 μm 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-Mβ images.

Fig. 7 shows typical ceramographs and X-ray images, U-Mβ for 40 mol% UO_2 and Th-Mα for 60 and 80 mol% 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% UO_2 pellets and the pore size are very large (above ~10 μm). The worst of the inhomogeneity is observed for 60 mol% UO_2 pellets sintered in wet 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% UO_2 agrees with those for the composition dependences of the bulk density and the line broadening.

Sol-derived powders of $(Th,U)O_2$ has been prepared mainly by drying and milling ThO_2-UO_3 sols. The high sinterability of the sol-derived powder indicates that the the powder would be very active or have large surface area. In the present study, sol-derived powders were prepared by NH_4OH coprecipitating from ThO_2-UO_3 mixed sols, followed by wet milling and calcining. It was found that the sinterability for the solderived powders was clearly higher than for the powder derived from the mixed nitrate solutions. **Fig. 8** shows secondary electron images of two kinds of $Th_{0.9}U_{0.1}O_2$ powders derived from NH_4OH coprecipitates. The powders were annealed at 800 °C in 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 μm and 3 ~ 4 μm. 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 $(Th,U)O_2$ pellets at high temperature, selective evaporation of uranium from the surface of $(Th,U)O_2$ is an important problem, since vapour pressures of

uranium species over $(Th,U)O_2$ are higher than of thorium species. In particular, high temperature annealing in vacuum[10] or oxidizing atmosphere[11] causes remarkable decrease of uranium concentration near the surface, because vapor pressure of UO_2 is relatively high and diffusibility of uranium ions in $(Th,U)O_{2+x}$ lattice is higher than in stoichiometric $(Th,U)O_2$. It has been reported that the region which are observed in $(Th,U)O_2$ reaches to above several tens μm from the surface in vacuum or oxidizing atmosphere. The $(Th,U)O_2$ pellets with theoretical density of about 95 % were used. However, the selective evapolation of uranium from $(Th,U)O_2$ may be affected also by the microstructure, such as density, pore and grain structures. It is expected that the selective evapolation in high-density $(Th,U)O_2$ pellets would be low in amount, because rapid transport of uranium caused by internal evapolation in pores is probably neglected. **Fig. 9** shows a ceramograph at near surface of $Th_{0.6}U_{0.4}O_2$ pellet prepared from the sol annealed at 1650 °C in He-4%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 ThO_2 and $Th_{0.8}U_{0.2}O_2$. The sintered densities are summarized in **Table 2**.

In ThO_2, the sintered density can be clearly enhanced by water vapour. On the other hand, the sintered density of the 20 mol% UO_2 pellet is lower than that of the ThO_2 pellet, which indicates that the preparation of high-density $(Th,U)O_2$ pellets by the oxalate process would be very difficult and would need sintering at higher temperatures. For sintering at 1750 °C, the sintered density in He-4%H_2 is higher than in 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% UO_2 pellets was examined by EPMA observations. **Fig. 10** shows the as-polished surface and the U-Mβ 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 °C for 100 h in He-4%H_2. Consequently, the prereducing of uranium in the mixed nitrate solution with a reducing agent such as sodium folmaldehyde sulfoxylate[12], is necessary to obtain the $(Th,U)O_2$ pellets with good homogeneity.

4. DISCUSSION

The bulk densities of the mixed sol-derived $(Th,U)O_2$ 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 μm, 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 $(Th,U)O_2$ pellets with high density and good homogeneity. However, the preparation of $(Th,U)O_2$ pellets with high uranium concentrations from the sol-derived powder may not be recommended, because ThO_2-UO_3 mixed sols with high uranium concentration (above about 40 mol%) is very unstable so that much UO_3 precipitate[6], as mentioned in chap 2.1.1.

Sintering in wet atmosphere appears to be very suitable for preparation of $(Th,U)O_2$ 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[2] for UO_2 pellets sintered in H_2-N_2-H_2O at 1300 °C. They have reported that the sintered density increases with the increase of ratio $P(H_2O)/P(H_2)$. The ratio is related to oxygen potential $\Delta G(O_2)$ by

$$\Delta G(O_2) = 2\,RT\,\ln\{\,P(H_2O)/P(H_2)\,\} + 2\,\Delta G^0, \qquad (3)$$

where ΔG^0 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_2 increases with the increase of oxygen potentials of sintering atmospheres. On the other hand, high density ThO_2 microspheres with diameter of about 500 μm as fuel kernels in coated fuel particles for HTGR have been prepared by Yamagishi et al[3] using the sol-gel method. The ThO_2 gel spheres were sintered at 1300 °C in wet air contained H_2O of 0.4 ~ 100 %. They have found that the sintered density increased with the increase of the partial pressure of H_2O 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_2. 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 UO_2 is affected significantly by the non-stoichiometry. For hyper-stoichiometric UO_{2+x}, the increase in oxygen interstitial concentration gives the rising of cation diffusion coefficient. Consequently, the sinterability of 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, ThO_2 is very stable compound and 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[13] have measured the diffusion of uranium and thorium in ThO_2-UO_2 solid solution at 1400 °C in the ranges of stoichiometry of 2.01 to 2.19 for 50 and 25 mol% 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 U^{+5}-O_i-U^{+5} defect complex. Consequently, it is expected that the sintering of $(Th,U)O_2$ pellets would be affected by the non-stoichiometrics, in the same manner as the sintering of UO_2 pellets.

Tentative phase diagram of Th-U-O system between 1250 and 1550 °C is shown in **Fig. 12**[14][15]. The main features of the diagram can be summarized as followed:

1. MO_{2+x} phase (face-centered cubic) is very stable in the ThO_2-rich region of above about 60 mol% ThO_2.

2. The MO_{2+x} phase is in equilibrium with U_3O_8 phase (orthorhombic) in the UO_2-rich (above 50 mol% UO_2) and high O/M (above 2.25) region.

As shown in fig. 5, the O/M ratio of $Th_{1-y}U_yO_{2+x}$ pellets in the UO_2-rich region (above 50 mol% UO_2) exceeds the permitted value, under which the MO_{2+x} phase is stable. Therefore the $Th_{1-y}U_yO_{2+x}$ pellets would be composed of $(Th,U)O_2$ and U_3O_8 phases. **Fig. 13** shows mean valences of uranium V_u, calculated from the O/M ratios, by using the relation[16]

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

The mean valence has a maximum at about 50 mol% UO_2. On the other hand, the inhomogeneity of composition would be prominent at a composition of about 50 mol% 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%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 $(Th,U)O_{2+x}$ phase can be stable, can enhance the sinterability, but strong oxidizing ones, in which the $(Th,U)O_{2+x}$ and U_3O_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_2O (g, 95 °C)	1500	-113
$He-4\%H_2/H_2O$ (g, 20 °C)	1500	-293
$He-4\%H_2$	1500	-473
	1750	-469

Table 2 Green and sintered densities of oxalate-derived pellets

UO_2 concentration (mol%)	Green density (%T.D.)	Sintered density (%T.D.)			
		1500 °C		1750 °C	
		Air	Air/H_2O	$Ar-4\%H_2$	$He-4\%H_2$
0	57.0	91.2	96.5	--	--
0.5	56.8	94.2	--	--	--
20	50.4	57.8	--	89.2	92.7

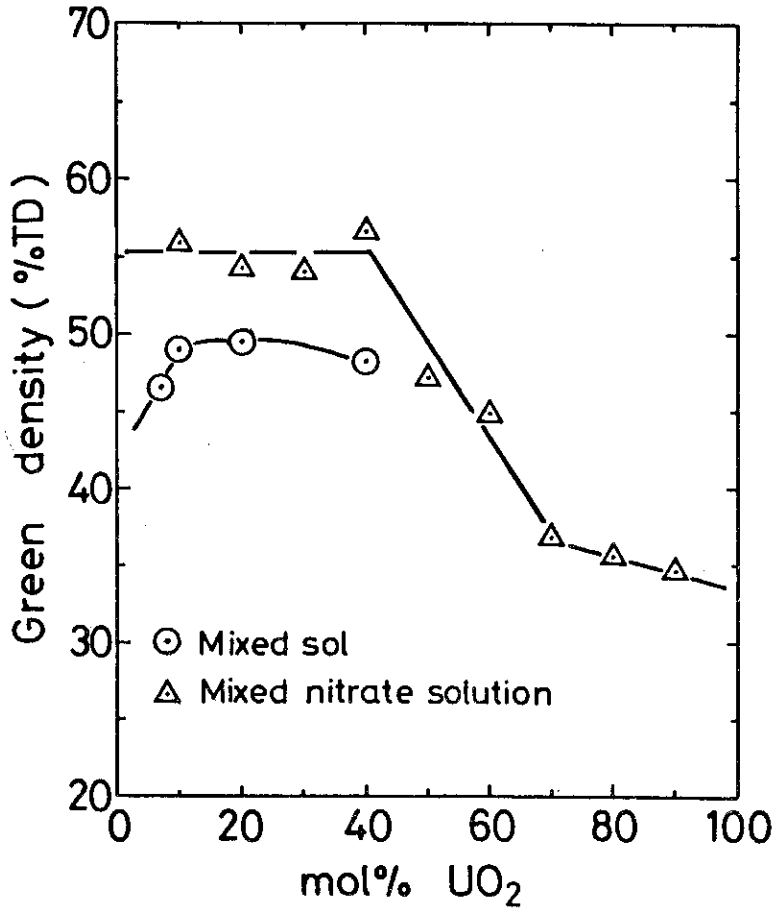

Fig.1 : Green densities of $(Th,U)O_2$ pellets derived from NH_4OH coprecipitates

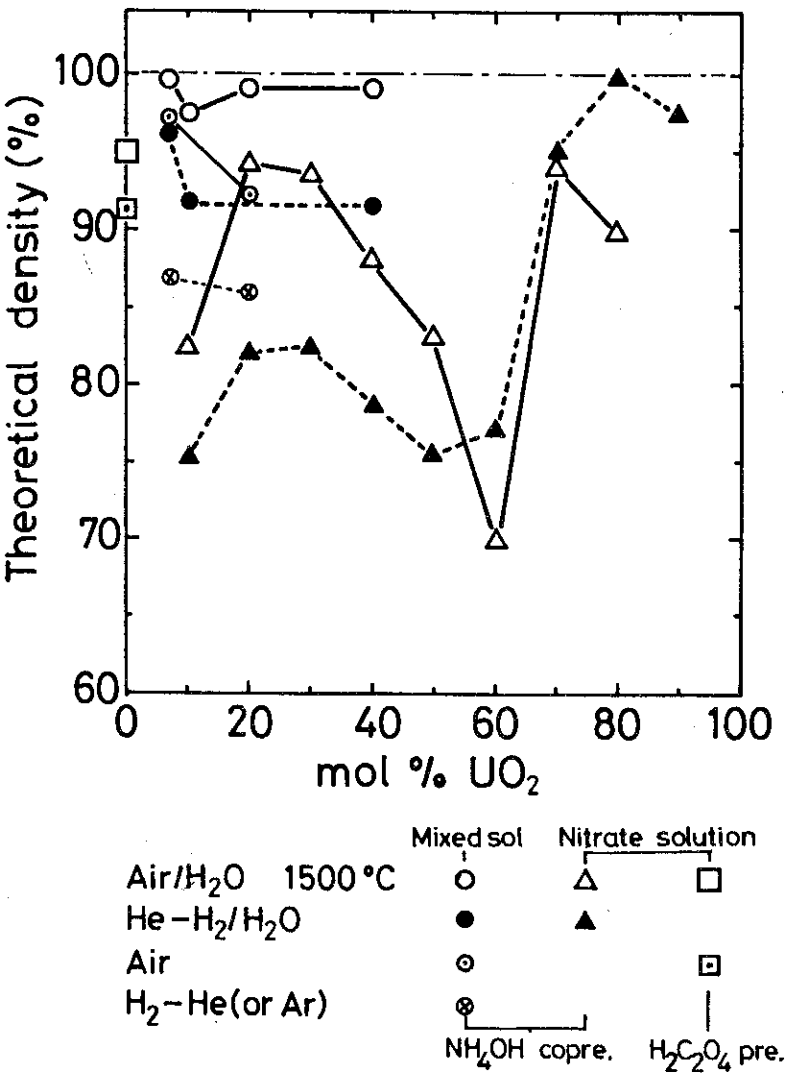

Fig.2 : Sintered density variations on powders, sintering atmospheres and compositions

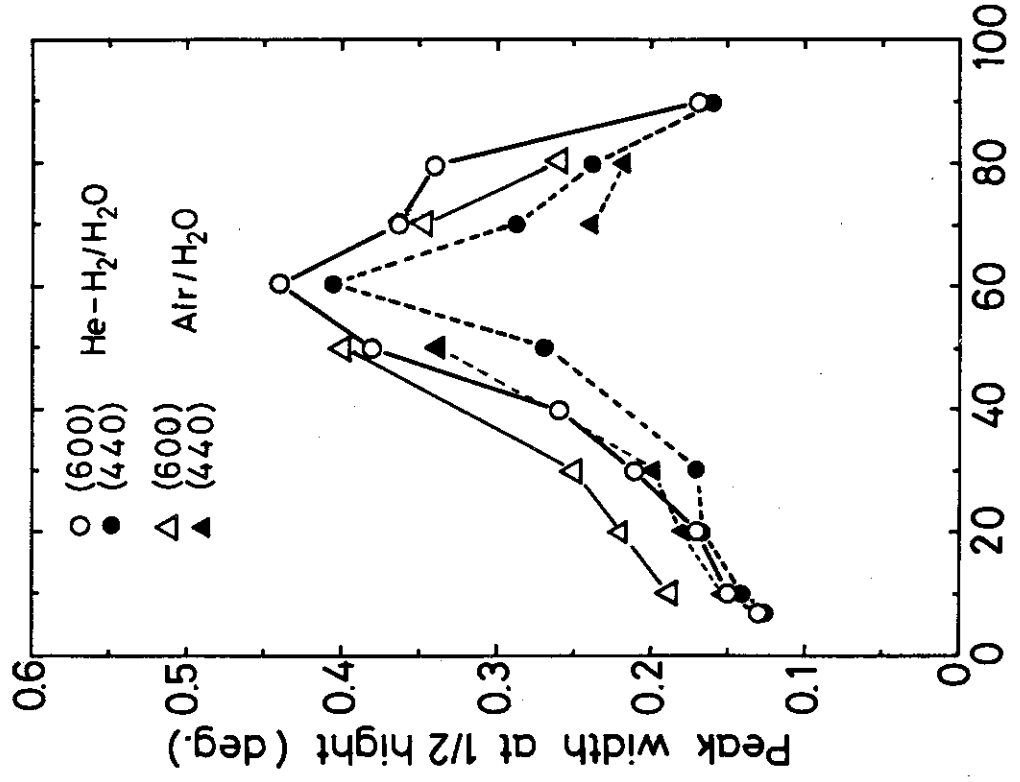

Fig.4 : Composition dependences of half widths of (600) and (440) diffraction peaks in sintered pellets

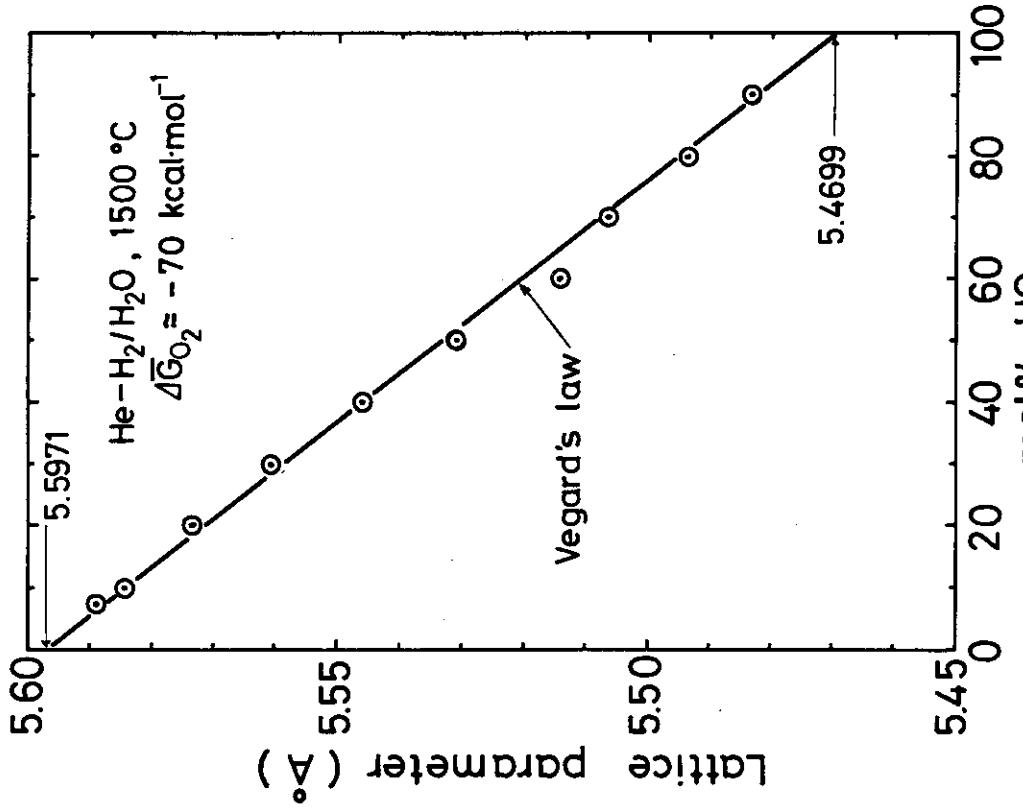

Fig.3 : Lattice parameter-composition curve in near stoichiometric (Th, U)O_2 pellets

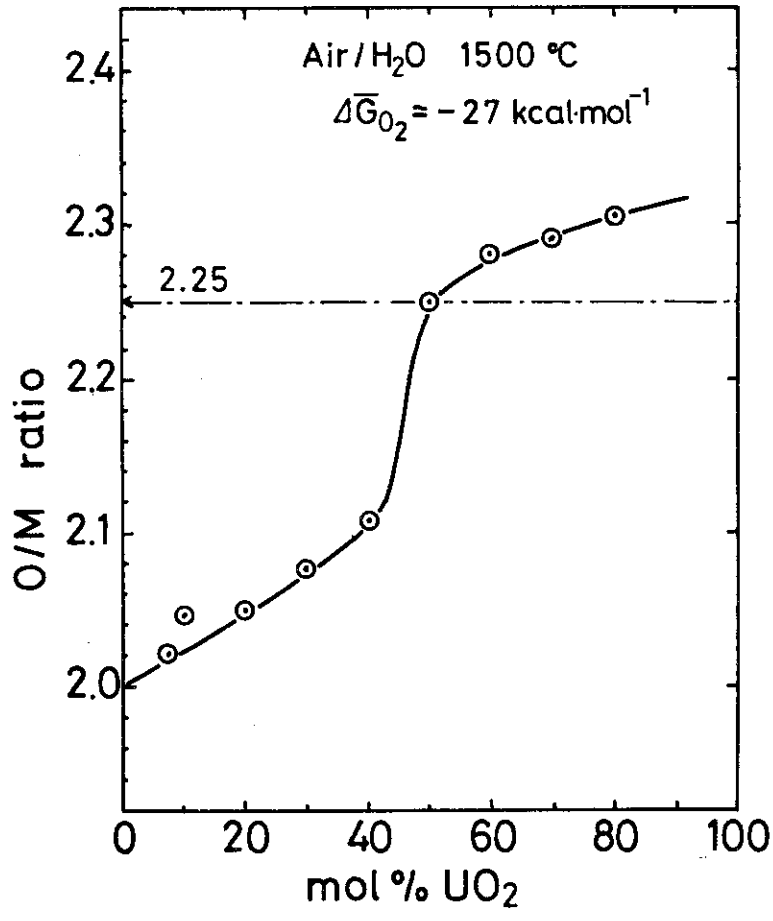

Fig.5 : Composition dependence of O/M ratios in pellets sintered in wet air

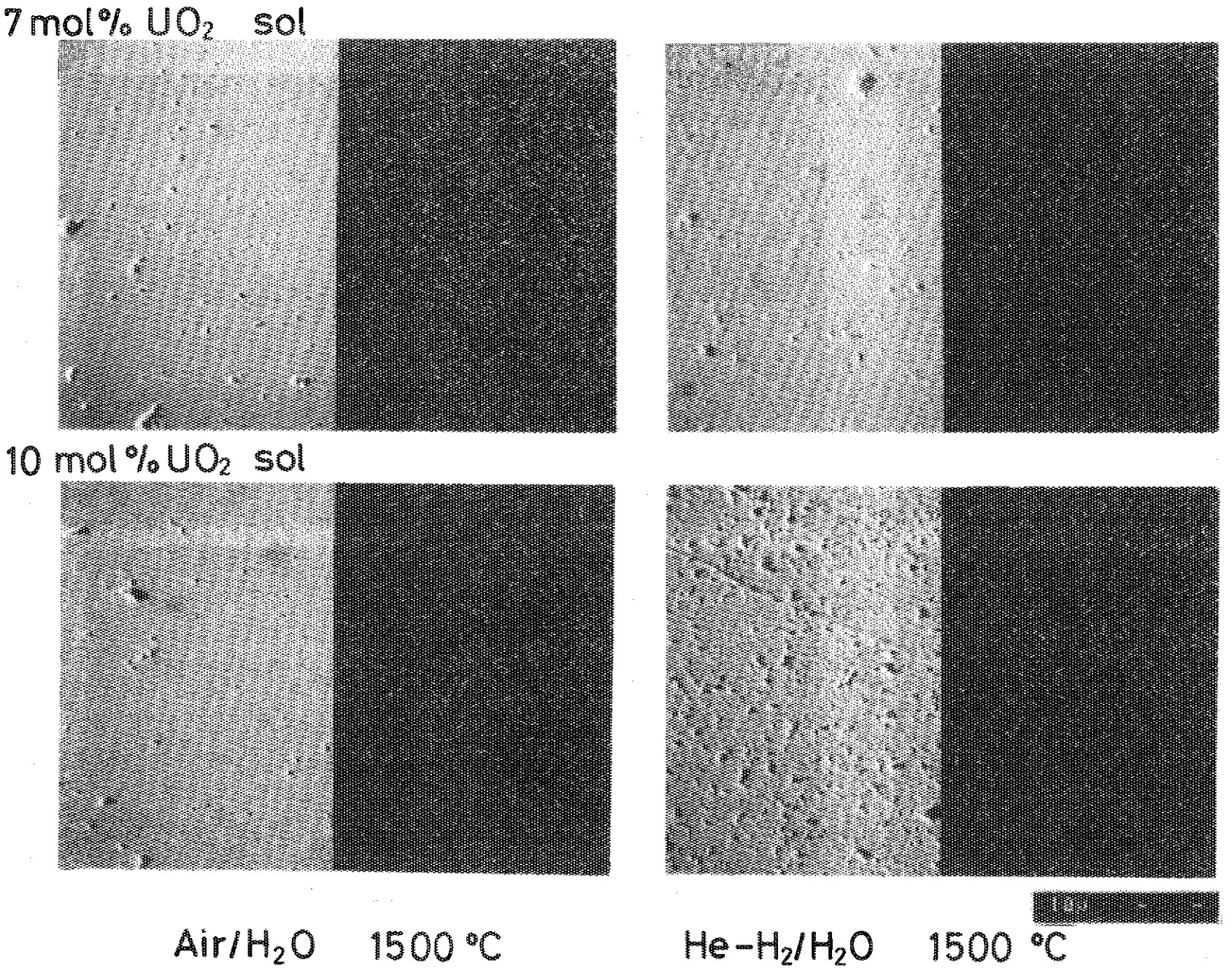

Fig.6 : Ceramographs and U-Mβ X-ray images of sol-derived pellets sintered in wet atmospheres

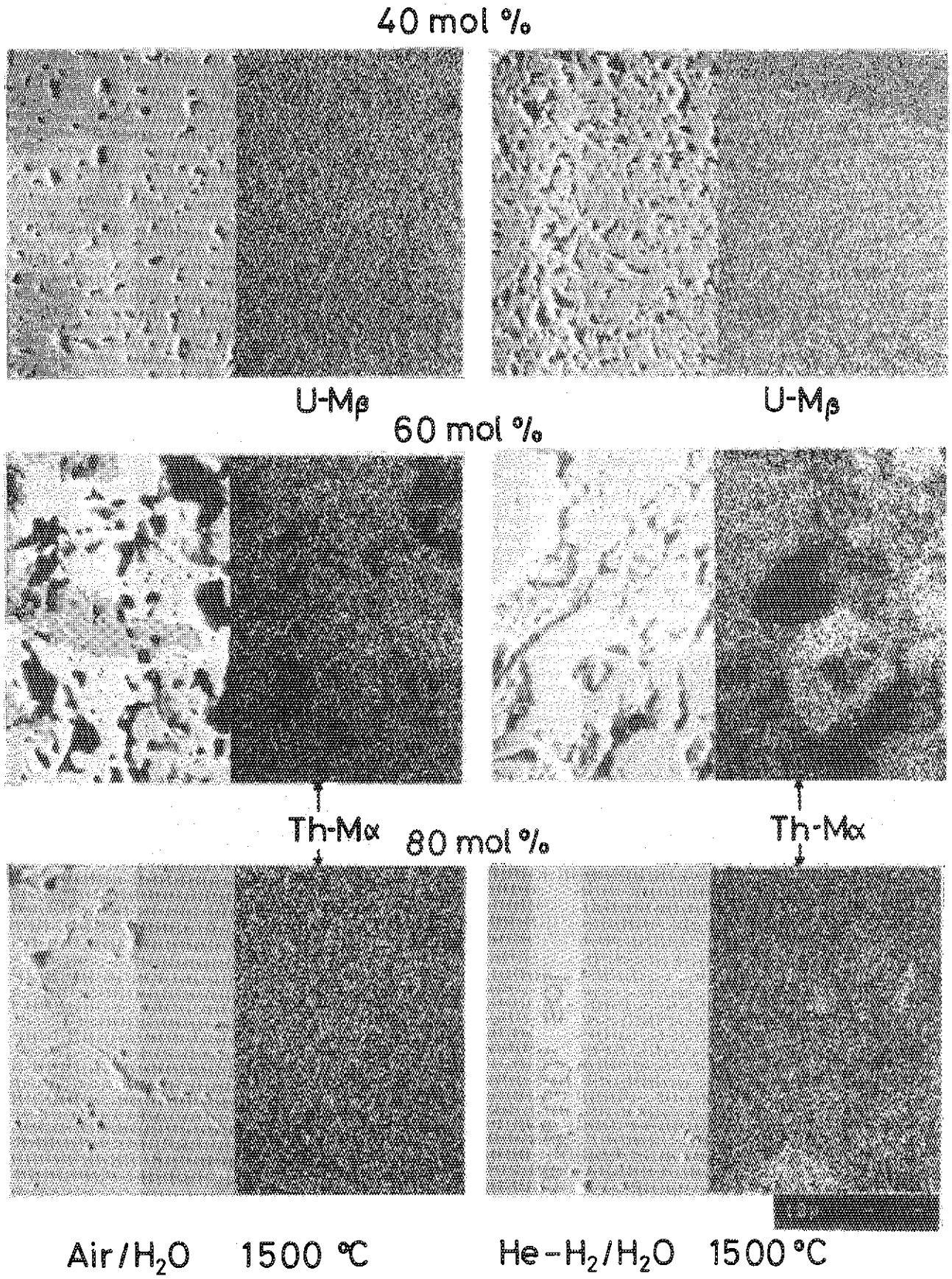

Fig.7 : Typical ceramographs and X-ray images of nitrate-derived pellets sintered in wet atmospheres

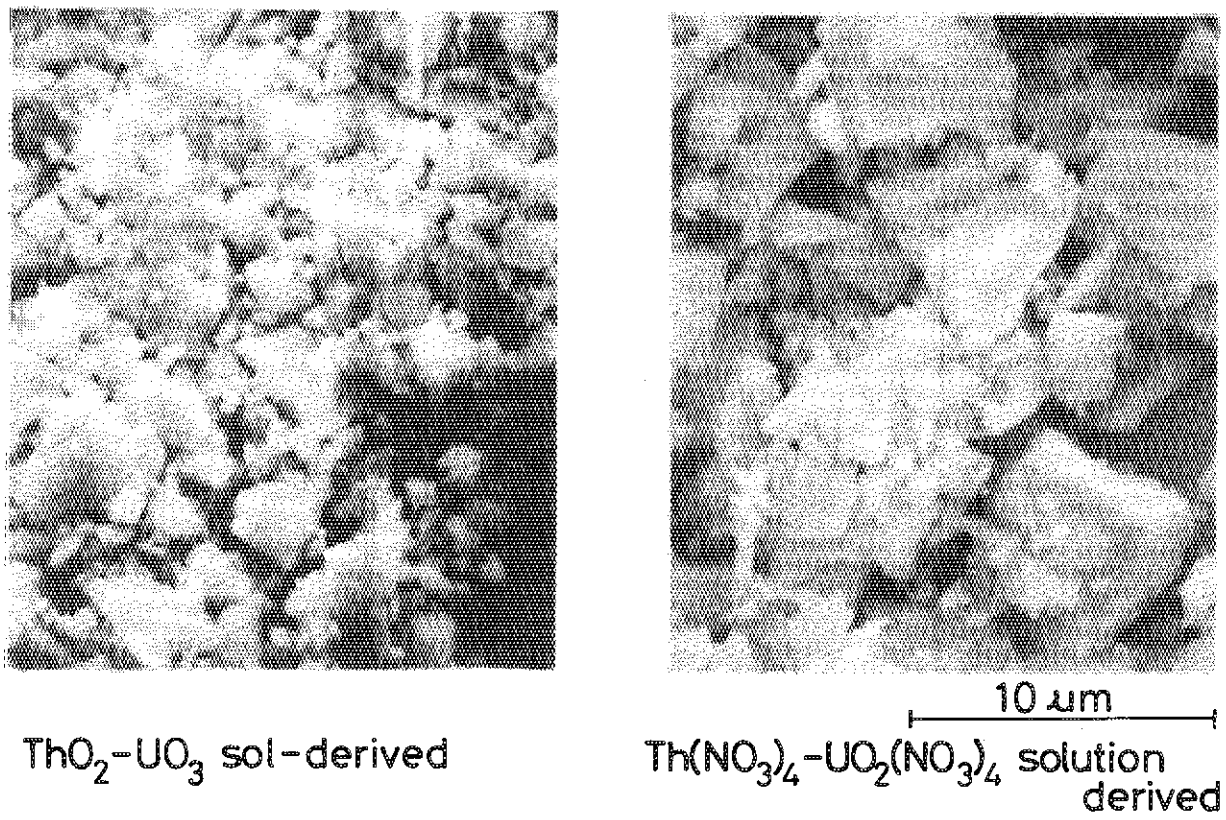

Fig.8 : Secondary electron images of 10 mol% UO_2 coprecipitates derived from the sol and the nitrate

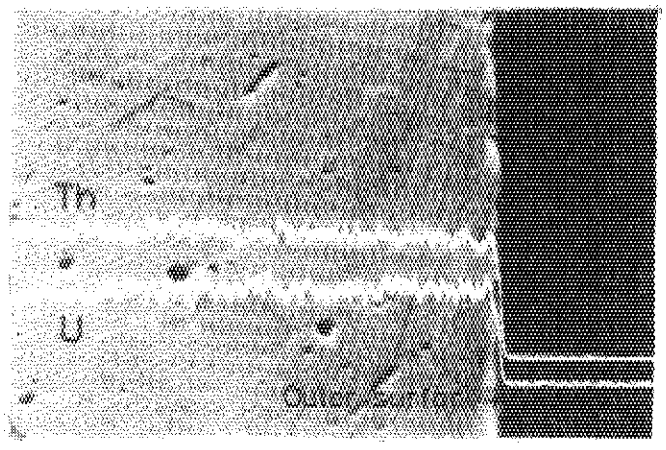

Fig.9 : Ceramograph at the near surface of a $Th_{0.6}U_{0.4}O_2$ pellet derived from the sol and annealed at 1650 °C in He-4%H_2 for 15h.

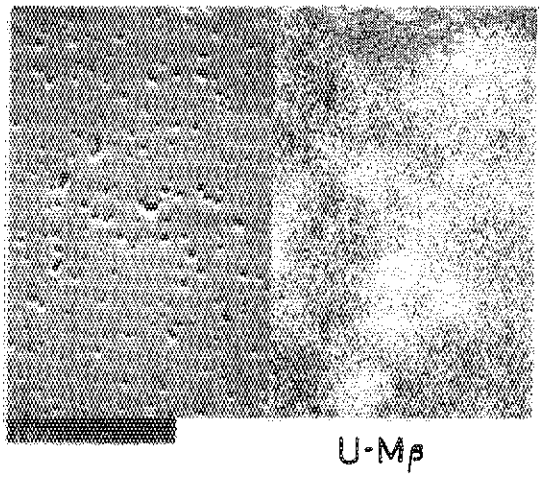

Fig.10 : U-Mβ X-ray images of a oxalate -derived $Th_{0.8}U_{0.2}O_2$ pellet

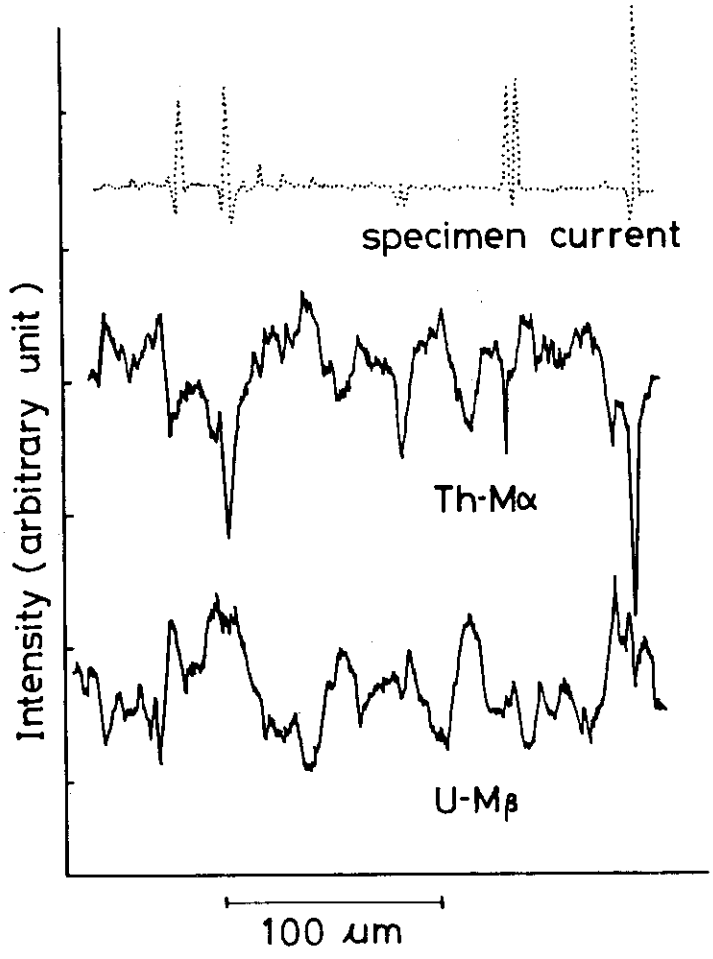

Fig.11 : X-ray line scannings of the oxalate-derived pellet

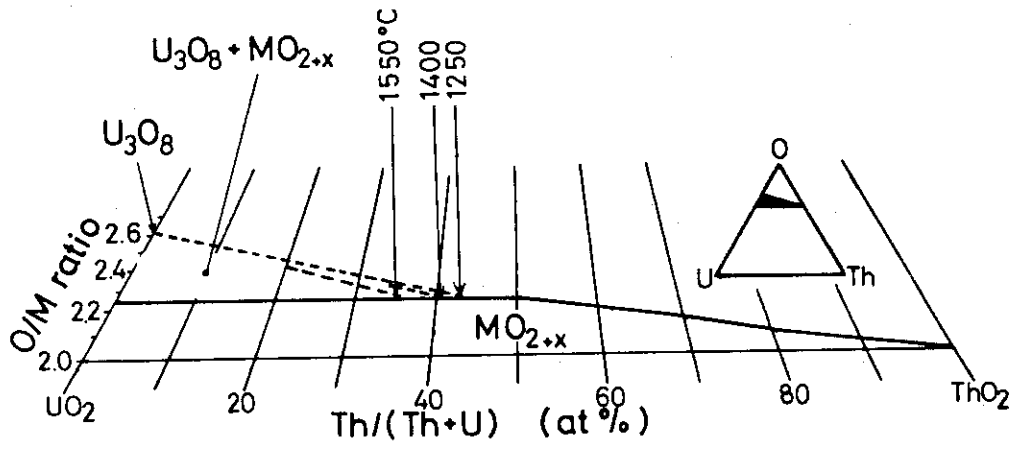

Fig.12 : Tentative phase diagram of Th-U-O system between 1250 and 1550 °C

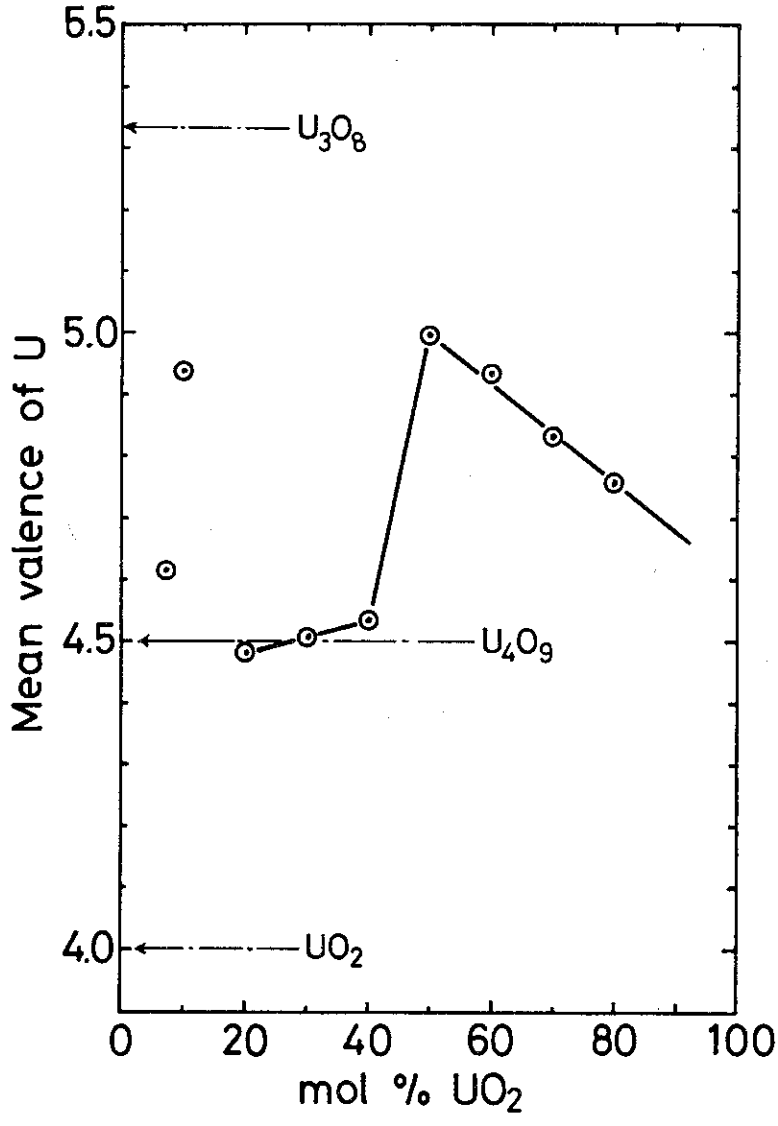

Fig.13 : Composition dependence of mean uranium valences in pellets sintered in wet air