# Phase Study of the System UO$_2$-Dy$_2$O$_3$

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## Abstract

The pseudo-binary system $UO_2$-$Dy_2O_3$ was prepared by heat-treatment in a helium atmosphere at 1100° to 2100°C, and studied by means of X-ray diffraction and metallography.   A Fluorite-structure solid solution was formed up to $DyO_{1.5}$ content of 55 to 65 mole %, depending on the temperature.   An intermediate phase with body-centered cubic structure, different from the so-called C-form $DyO_3$, was observed, extending to the more uranium-rich region at higher temperature.   This phase is considered to be an ordered structure of the fluorite-type solid solution, accompanied by a change of the O/M ratio.

Between this and the C-form $Dy_2O_3$ phase, there exists a broad two-phase region, extending from about 70 to 90 mole % of $DyO_{1.5}$, depending on the temperature.

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# UO₂-Dy₂O₃ 系 の 相 研 究

## 要　　旨

擬二元素 $UO_2$-$Dy_2O_3$ をヘリウム中, 1100°C～2100°C で熱処理して調製し, X線回折および顕微鏡観察を行なった. $DyO_{1.5}$ の成分比が 0 から 65 mole % では螢石型構造の固溶体が形成され, さらに 60～70% の範囲では中間相の単相領域がみられた. この中間相は b.c.c. 構造で, 螢石型固溶体の一種の規則状態と考えられ, その存在範囲は高温になるほど $UO_2$ 側に広がることが見出された. この中間相と $Dy_2O_3$ 相の間には 70～90% にわたってかなり広い二相領域がみられた.

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# 1. Introduction

The dysprosium oxide $Dy_2O_3$ is dispersed in the $UO_2$ fuel for light-water moderated reactors in order to suppress a flux peaking at the core center and to use as a burnable poison. From this standpoint, the ternary or pseudo-binary system $UO_2$-$Dy_2O_3$, as well as other rate earth oxides, have been studied by several workers.

PLOETZ[1] studied the specimens hydrogen-sintered at 1750°C by X-ray diffraction, and reported that f.c.c. solid solution was formed up to at least 70 wt % $Dy_2O_3$ with the lattice parameter decreasing according to Vegard s' law, and that beyond 70% there was a two-phase region; though the nature of the second phase was not clarified.

KOSHCHEEV et al.[2],[3] made extensive studies on the phase of uranium oxide-rare earth oxide system, mainly higher oxides than $UO_2$; in $UO_2$-$R_2O_3$ (R being rare earth elements), they examined specimens vacuum-treated at 1700° and 1800°C, and suggested the existence of a body-centered cubic phase different from the C-form rare earth oxide phase which is b.c.c. in the metallic elements. These results differed from the Ploetz's in the extent of fluorite phase region and the decrease rate of a lattice parameter in it.

From the nature of rare earth elements, close relationship is expected between various $UO_2$-$R_2O_3$ systems, R is rare earth element with similar atomic number. Relatively many reports[4],[5],[6] have been made on system $UO_2$-$Gd_2O_3$, and $UO_2$-$Eu_2O_3$, the results all agree in the extensive fluorite region existing on the uranium-rich side, but not in the rare earth rich region. In the case of $Gd_2O_3$ and $Eu_2O_3$, the B-form (monoclinic) solid solution covers a large region, and its boundary with the cubic phase is a main problem in phase studies. As dysprosium oxide has C-B transformation temperature much higher than for gadlinium and europium oxide,[7] B-form solid solution would be confined to the higher temperature region rich in dysprosium. Therefore, most of the phase diagram is thought to be composed of cubic phases. Dysposium oxide has a $Mn_2O_3$ type structure (b.c.c. as regards dysprosium) with the lattice parameter about twice that of $UO_2$ which has a fluorite type structure (f.c.c as regards uranium). The lattice planes of both structures correspond to each other, as shown in TABLE 1. The f.c.c. to b.c.c. transition with a doubling of lattice parameter is a typical example of the order-disorder phenomenon. Then, the phase transformations in this system are expected to have features similar to the order-disorder transformations. The present study was aimed at the general survey of the system with emphasis on the order-disorder phenomenon.

TABLE 1 Corresponding lattice planes of $UO_2$ and $Dy_2O_3$
that have intensity factors greater than 10

| $UO_2(a=5.472Å)$ | | | $Dy_2O_3(a=10.66Å)$ | | |
|---|---|---|---|---|---|
| h kl | $I/I_0$ | $2\theta$(Cu-$K_\alpha$) | h kl | $I/I_0$ | $2\theta$(Cu-$K_\alpha$) |
| | | | 2 11 | 15 | 20.40 |
| 1 11 | 100 | 28.24 | 2 22 | 100 | 28.97 |
| 2 00 | 48 | 32.72 | 4 00 | 40 | 33.59 |
| | | | 5 10 | 11 | 43.23 |
| 2 20 | 49 | 46.94 | 4 40 | 45 | 48.24 |
| 3 11 | 47 | 55.69 | 6 22 | 35 | 57.24 |
| 3 31 | 18 | 75.72 | 6 62 | 11 | 78.04 |

## 2. Experimental

Specimens were prepared from reactor-grade $UO_2$ powder from Mitsubishi Mining Co. and $Dy_2O_3$ powder of 99. 9% purity from Michigan Chemical Co. The two kinds of powder were mixed at 5 mole % intervals of $DyO_{1.5}$ content (at 10% intervals from 70 to 100%). The mixture was then pressed at 3 tons/cm² and sintered in purified helium at 1750°C for 2 hours. Specimens were then heat-treated in purified helium at different temperatures; 2100°C for 1 hour (A-group), 1900°C for 2 hours (B-group), 1100°C for 15 hours (C-group). Then, specimens were furnace-cooled as rapidly as possible. Some of the B-group specimens were additionally heat-treated in hydrogen atmosphere at 1600°C for 2 hours. The temperature was measured with a micro-optical pyrometer.

X-ray diffraction was made on powdered specimens with Cu-K$\alpha$ radiation, using goniometer. Lattice parameters were obtained from peaks with $2\theta$ 100° to 150°, using $\cos^2\theta$ extraporation for the specimens in the fluorite region. The solid solutions rich in dysprosium had weak high-angle peaks so that the lattice parameters were derived from low-angle peaks ($2\theta$ equals about 80°) using silicon powder as an internal standard. Samples for metallography were prepared by polishing of the sintered specimen mounted in resin with number 220 to 1000 emery papers, buff polishing with 3 microns diamond paste and chemical etching. $1 H_2SO_4 + 9 H_2O_2$ solution was used for etching in the fluorite region, while 50% HCl solution used for specimens rich in dysprosium. In the intermidiate compositions both etching agents were successively applied.

The oxygen to metallic atom ratio was measured for B-group specimens by weighing before and after heating in air at 900°C for 4 hours.

## 3. Results

Three typical examples of X-ray diffraction pattern are shown in Fig. 1 (a) to (c). Only cubic structures were present in the composition range examined, and therefore the three patterns are nearly the same. Together with the results of lattice parameter measurement and micro-photography, these three are considered to show three areas, i. e. (a) fluorite type structure near $UO_2$ (b) unidentified intermediate area, and (c) C-form rare earth oxide phase, The diffraction pattern in Fig. 1 (a) is basically the same as that for $UO_2$, although the intensities of diffraction peak gradually decrease with the dysprosium content. In Fig. 1 (b) and (c), the intensities of high-angle peaks are remarkably low, compared with those in Fig. 1 (a). Diffraction peaks corresponding to the (510) or (541) of $Dy_2O_3$ are observed in Fig. 1 (c). It is impossible for these peaks to appear in the fluorite structure, so that their appearance means that the lattice parameter two times that of the fluorite structure must be taken. In Fig. 1 (b), these super lattices of the fluorite structure are not clearly observed as in Fig. 1 (c). In other respects there were seen no marked differences. The classification of diffraction patterns in Fig. 1 (b) and 1 (c) is not a definite one: it is only intended for the convenience of the later discussion on the results of lattice parameter measurement and microphotographs. On the other hand, the difference of (a) and (b) from (c) was fairly distinct, and it was found that

(a) 0.50 UO₂-0.50DyO₁.₅ A-group (Cu-Kα)

(b) 0.35UO₂-0.65DyO₁.₅ A-group (Cu-Kα)

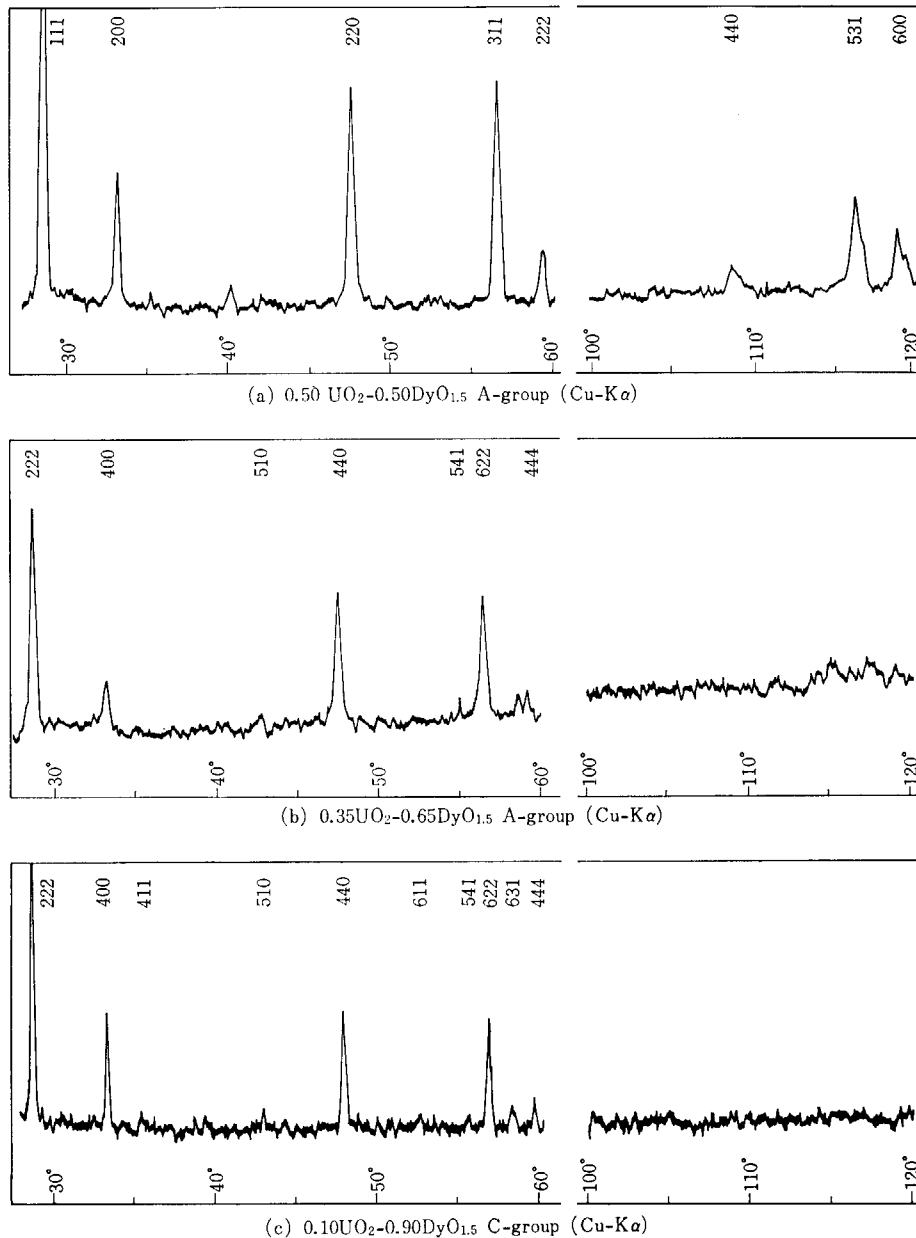(c) 0.10UO₂-0.90DyO₁.₅ C-group (Cu-Kα)

Fig. 1  Examples of X-ray diffraction chart

the diffraction pattern (a) covered the dysprosium content range of 0 to 55% in A-group, 0 to 65% in B-group, and 0 to 60% in C-group specimens.

The lattice parameters of three groups of specimen are shown in **Fig. 2** as a function of the dysprosium content.    Since the lattice parameter of dysprosium oxide is about twice that of uranium dioxide, the lattice parameter is expressed in 1/2 in the b.c.c. region, to make clear the relation with fluorite region.    At 0 to 55%, each group of specimens showed the same behaviour ; the lattice parameter decreased from 5.472 Å to 5.356 Å following Vegard's law. In A-group (annealed at 2100°C), the lattice parameter showed a discontinuous increase to 5.405 Å at 60%.    The diffraction pattern also changed at this composition from that in **Fig. 1** (a) to **Fig. 1** (b).    From 60 to 70%, the lattice parameter again decreased linearly to 5.386 Å, with the diffraction patterns nearly alike.    These measurements were made immediately after their preparation.    The re-measurement five months later, however, showed decreases in the lattice parameter, as shown by arrows in the figure, for 60 and 65% specimens of A-group.    The

diffraction pattern had also changed to the one shown in **Fig. 1** (a), no such change was observed at 70%.

B-group specimens (annealed at 1900°C) showed a constant lattice parameter of 5.351 Å at 60 to 65% and made no change after four months at room temperature; their diffraction pattern was similar to that shown in **Fig. 1** (a). At 70%, lattice parameter showed a discontinuous increase to 5.388 Å accompanying a change in diffraction pattern like that between 55 and 60% of A-group. At 80%, diffraction peaks were broad and strongly distorted, so that the derivation of lattice parameter was difficult. 90% specimen showed similar patterns to those for dysprosium oxide.

C-group specimens (annealed at 1100°C) showed a constant lattice parameter of 5.356 Å at 55 to 60%, which coincided with that of A-group after the change described already. The lattice parameter increased discontinuously to 5.396 Å at 65% accompanying a change of diffraction pattern, as described for A- and B-group. At 70 to 80%, constant values of lattice parameter were observed. At 90%, as in B-group, the diffraction pattern was like that of dysprosium oxide.

In **Fig. 2** are also shown the results of an additional heat treatment to B-group specimens in hydrogen atmosphere at 1600°C for 2 hours. This heat treatment caused a change of the lattice parameter from 5.351 Å to 5.400 Å at 60%, contrary to the case observed for A-group specimens at room temperature. It was found that all the specimens which had the diffraction pattern shown in **Fig. 1** (a), had the lattice parameters on the straight line in **Fig. 2** and its horizontal branches.

**Figs. 3** to **5** are microphotographs of the etched surface of the specimens; **Fig. 3** shows microstructures of the specimens considered to have fluorite structure. It is seen that the more porous becomes the structure the higher the dysprosium content. This feature was common to each group up to 55% dysprosium content. Mesh-like patterns observed in **Fig. 3** (b) and (c) are considered to be micro-cracks which were formed during cooling to room-temperature. **Fig. 4** shows microstructures of eact group of specimens at 60 and 65% dysprosium content.
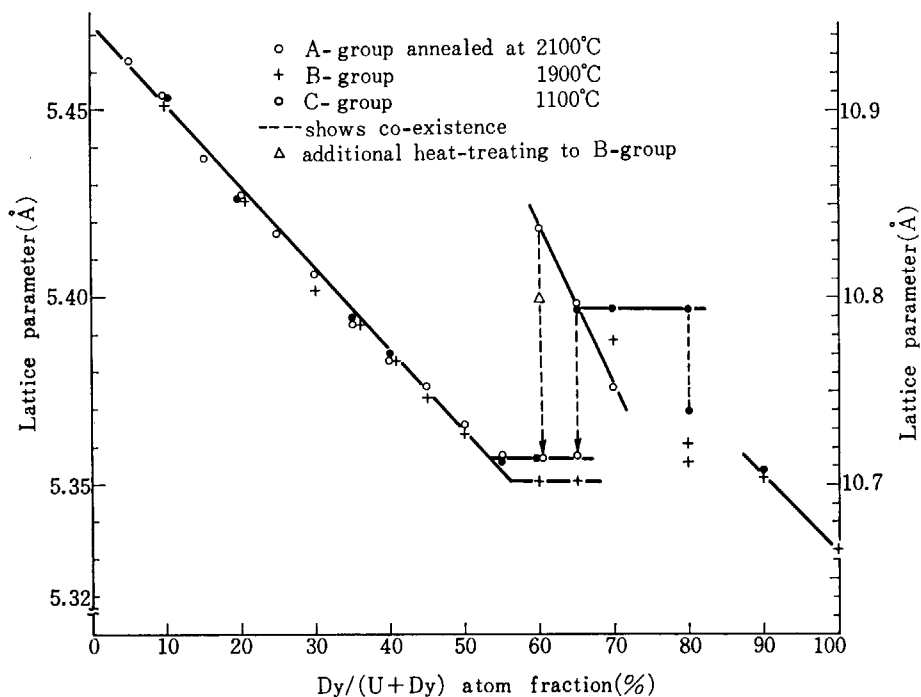


**Fig. 2** Lattice parameter variation as a function of dysprosium content.

(a)  $0.95\,UO_2$-$0.05\,DyO_{1.5}$       $10\,\mu$       (b)  $0.80\,UO_2$-$0.20\,DyO_{1.5}$

(c)  $0.60\,UO_2$-$0.40\,DyO_{1.5}$                 (d)  $0.50\,UO_2$-$0.50\,DyO_{1.5}$
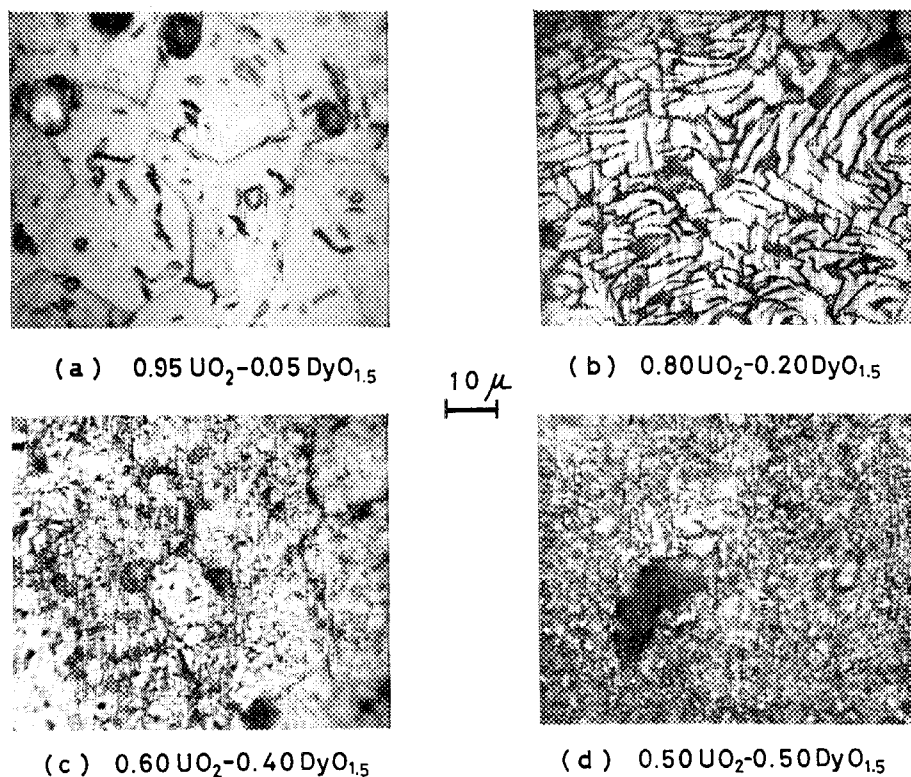
Fig. 3   Microstructure of specimens annealed at 2100°C
(A-group) in the uranium-rich region.

In B-group, porous and strongly distorted structure continues up to 65%, while in A-group, a dense structure appears at 60% which has an appearances different from that of dysprosium oxide.   In C-group, the dense structure appears at 65%.   These dense structures are considered to be the same single-phase, and it is obviously different from the fluorite-phase.   Because of the presence of a strongly porous structure, it was not possible to tell whether two-phase region existed between this phase and the fluorite phase or not.

Fig. 5 shows microstructures of B- and C-group specimens at 70 to 90%.   In Figs. 5 (b), (d) and (e), the existence of two phases is apparent, one of which, white portions in the photos, could not be etched by 50% HCl solution, while dark portions were easily etched as in the case of dysprosium oxide.   These white portions seem to be an extension of the dense single-phase appearing in Fig. 4 (a), (b), (f) and Fig. 5 (a).

The O/(U+Dy) atomic ratio of B-group specimens are shown in Fig. 6.   They were calculated by assuming that the final chemical form is $U_3O_8+Dy_2O_3$.   It is a conventional method in the case of $UO_{2\pm x}$, but in this case it is doubtful that oxidation proceeded completely to this state, so that there is a chance O/M values are overestimated.   For this reason, the measurement was made on only some of B-group specimens as a reference experiment.   In Fig. 6, the rapid decrease of O/M ratio at about 65% $DyO_{1.5}$ is remarkable.
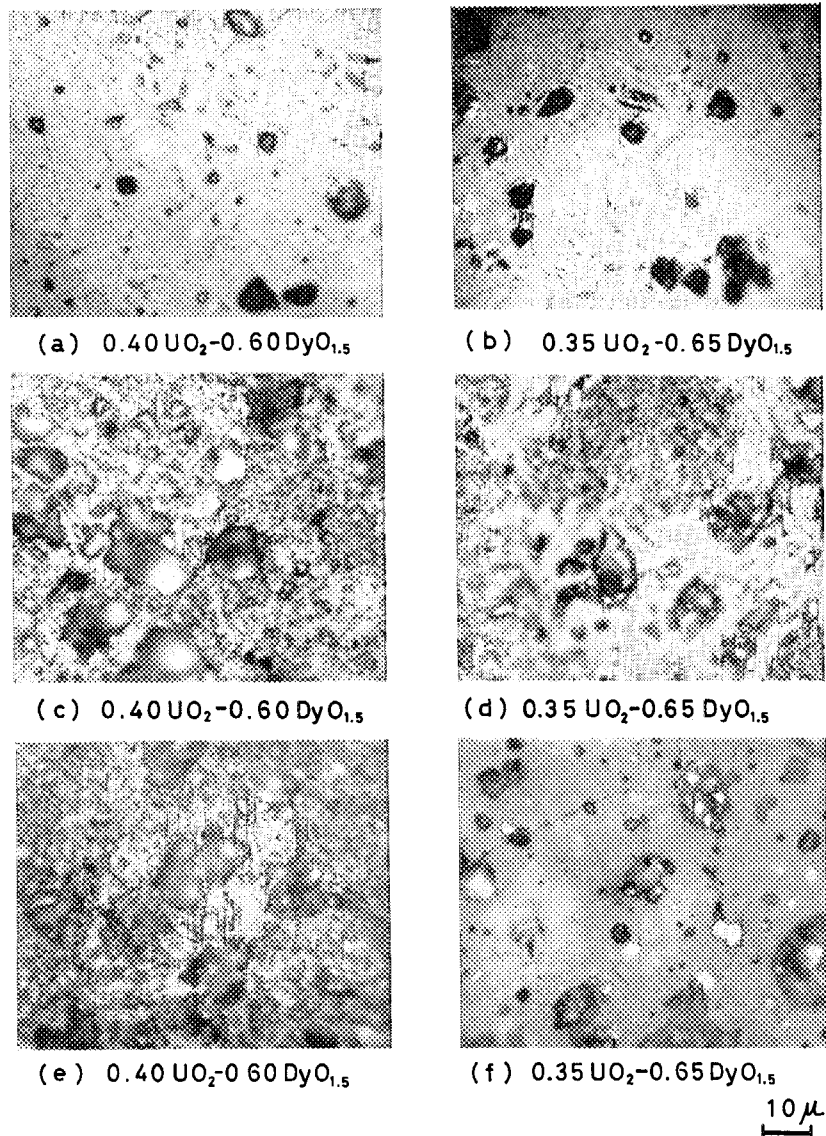
(a)   0.40 UO₂-0.60 DyO₁.₅



(b)   0.35 UO₂-0.65 DyO₁.₅



(c)   0.40 UO₂-0.60 DyO₁.₅



(d)  0.35 UO₂-0.65 DyO₁.₅



(e)   0.40 UO₂-0 60 DyO₁.₅



(f)  0.35 UO₂-0.65 DyO₁.₅

10 μ

Fig. 4   Microstructure of specimens in the intermediate compositional range.
(a), (b) A-group    (c), (d) B-group    (e), (f) C-group

## 4.  Discussion

In the studies performed, the data of X-ray diffraction pattern, lattice parameter and microphotographs were supplementary to each other in various composition ranges, in determining to what phase each specimen belonged. Data of lattice parameter were effective in the region rich in uranium, whereas in the region rich in dysprosium, they were rather too complicated and confused.   On the contrary, microphotographs gave clear results in the dysprosium-rich region, while in the region where the dysprosium content is less than 50%, microstructures were strongly porous and it was difficult to deduce any conclusion.

From diffraction pattern alone, the whole system is divided into two regions and the boundary between them lies at 55% to 70% DyO₁.₅ accompanying a discontinuity of volume. Another division, however, is apparent from **Fig. 5**, in which the presence of two phases is clearly observed.   One of them, dark portions in the photos, undoubtedly continues to the C-
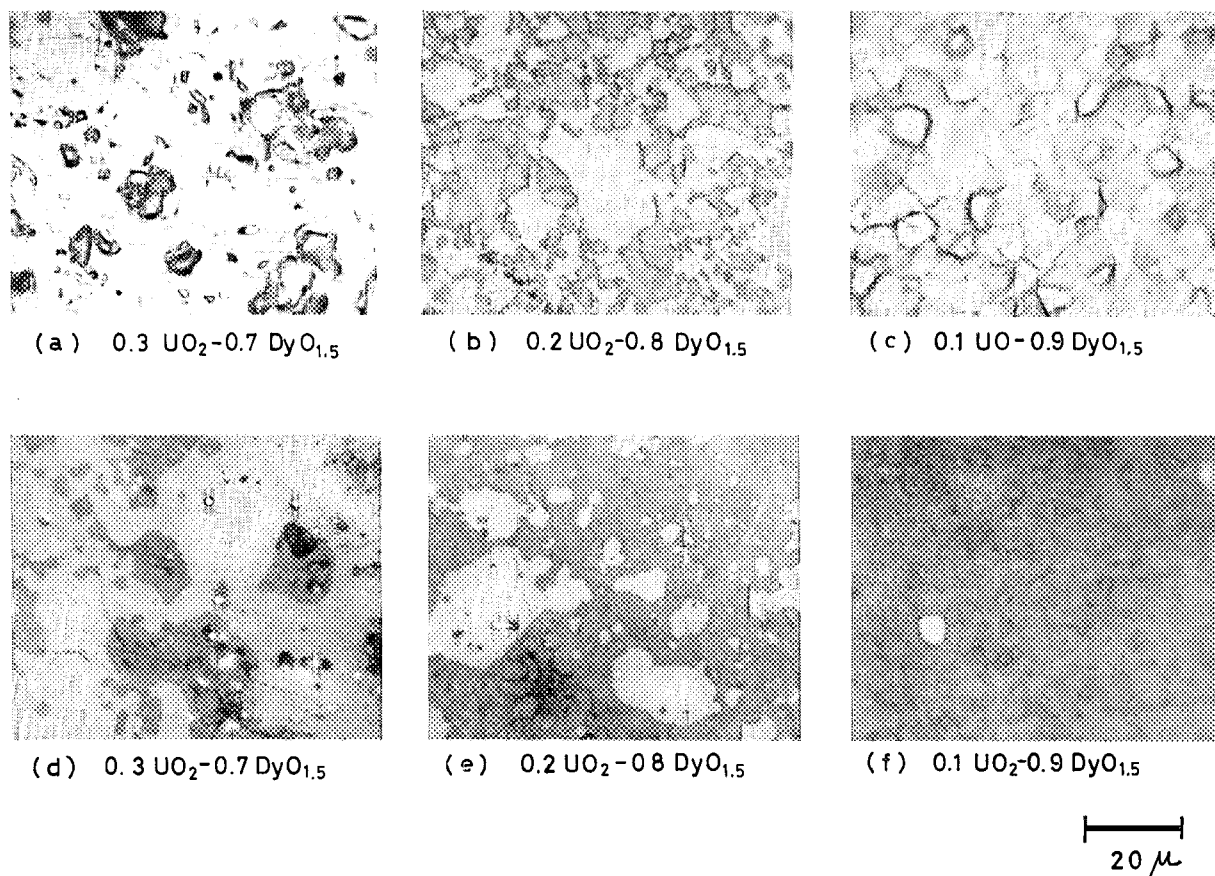
(a)   0.3 UO₂-0.7 DyO₁.₅         (b)   0.2 UO₂-0.8 DyO₁.₅         (c)   0.1 UO-0.9 DyO₁.₅

(d)   0.3 UO₂-0.7 DyO₁.₅         (e)   0.2 UO₂-08 DyO₁.₅          (f)   0.1 UO₂-0.9 DyO₁.₅

$\longmapsto$
20 μ

**Fig. 5**   Microphotographs showing coexistence of two phases.
(a)-(c) B-group        (d)-(f) C-group
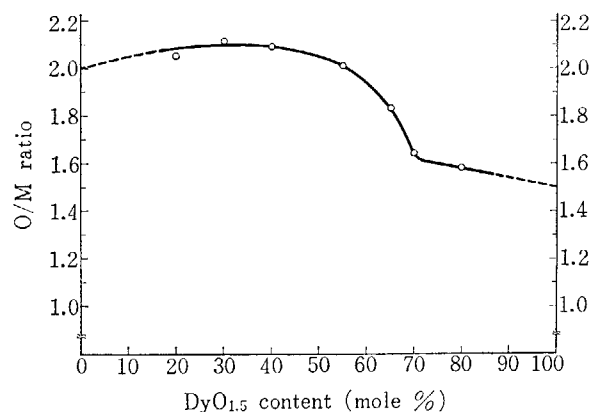


DyO₁.₅ content (mole %)

**Fig. 6**   Variation of O/M ratio in specimens
annealed at 1900°C.

form rare earth oxide phase, which is etched by HCl solution at boiling temperature. Another one, white portions in the photos, is considered to have a continuity on the single-phase region observed around 65% DyO₁.₅, i. e. **Fig. 4** (a) and (b) for A-group, **Fig. 5** (a) for B-group and **Fig. 4** (f) for C-group specimens. They could not be etched by HCl solution. Therefore, it may be safely said that there are at least three different single phases in the range examined in this experiment.

The first one near UO₂ is undoubtedly a fluorite phase. The lattice parameter data approximately follow Vegard's law in every group of specimens up to at least 55% DyO₁.₅. This behaviour is in agreement with KOSHCHEEV et al.'s results. The region of constant lattice

parameter observed in **Fig. 2** at about 55% $DyO_{1.5}$ is also considered to be fluorite structure. The reason why two levels of constant lattice parameter were observed will be discussed later, with reference to KOSHCHEEV *et al.*'s results.

As mentioned above, the existence of the intermediate phase and its difference from C-form rare earth oxide phase could not be shown in a straightforward way. Its existence is deduced from the observation of a two-phase region which is evidently different from that of lattice parameter discontinuity in **Fig. 2**. At 60 to 70% $DyO_{1.5}$ in A-group, the lattice parameter shows an approximately linear decrease as a function of the dysprosium content. This behaviour is thought to give an evidence of the existene of this phase. The X-ray diffraction pattern of the phase was similar to that of $Dy_2O_3$ in that the intensities of high-angle peaks were extremely low but super lattice lines corresponding to (211) or (510) of $Dy_2O_3$ were much weaker than in $Dy_2O_3$ phase, and at 60% in A-group it was almost impossible to tell whether these lines existed or not. In spite of this fact, however it will be appropriate to assume that this phase has a body-centered cubic structure with lattice parameter about 10.8 Å, i. e. about twice that of $UO_2$. This phase is considered to be stable at higher temperature, from comparison of the results of annealing at different temperatures and from the fact that two specimens of A-group showed a transformation from this phase to the fluorite phase at room temperature.

**Fig. 7** shows the difference between the results obtained and KOSHCHEEV *et al.*'s also concerning the interpretations. Present results are shown by solid lines while KOSHCHEEV *et al.*'s by dotted lines. They reported the coexistence of two phases A and $A_2$, both a fluorite structure with constant lattice parameter. From the present results, it is seen that there are four levels at which the fluorite solid solution has a constant lattice parameter. Then, it would be more reasonable to assume that the fluorite solid solution stops shrinking at any dysprosium content, depending on the annealing conditions. They also reported of a b.c.c. phase as K-phase which was different from $Dy_2O_3$. It is considered to be identical with the intermediate phase found in the present experiment, though there are differences in lattice parameter values and also in the composition range in which the phase is situated. Therfore, information on the phase transformations in this system is obtained by putting together both results.
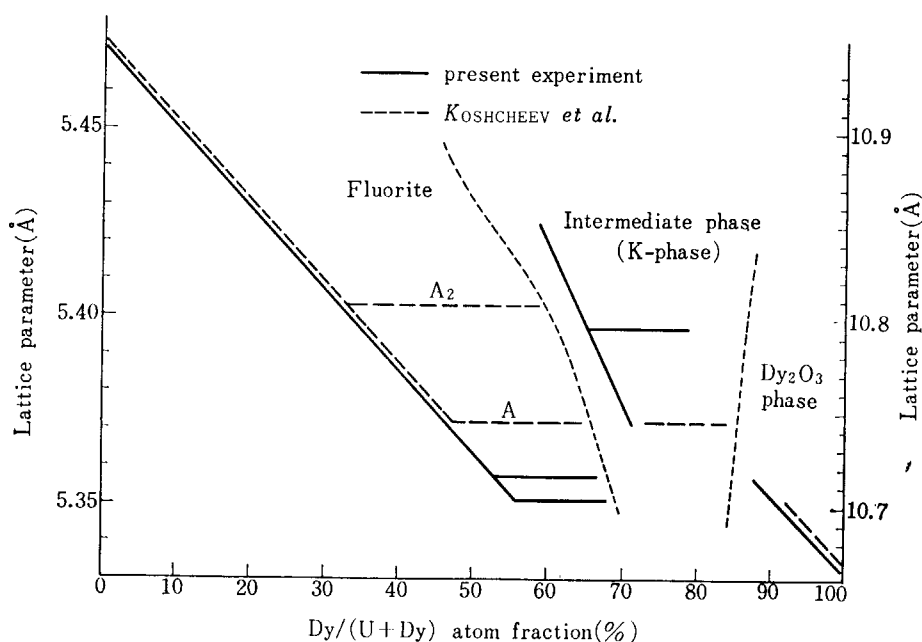


**Fig. 7**  Illustration of results and interpretation of the present and KOSHCHEW *et al.*'s experiments.

The present experiment is based on the concept of pseudo-binary system, that is, $UO_2$-$Dy_2O_3$ section of the ternary system U-Dy-O; many of the reports made on $UO_2$-$R_2O_3$ system (R being rare earth elements) are based on the same concept. In systems like this, however, it is very difficult to maintain the pseudo-binary condition, but this condition itself is not significant. As is observed in **Fig. 6**, the pseudo-binary condition i. e. linear variation of O/M ratio was not exactly realized in this experiment; that is, there are deviations in experimental points from $UO_2$-$Dy_2O_2$ section in the ternary phase diagram U-Dy-O, and problems of stoichiometry must be considered. Three types of stoichiometric composition are conceivable, $(U, Dy)O_2$, $UO_2$-$Dy_2O_3$, and $(U, Dy)_2O_3$. Crystallographically, the first one is a fluorite structure with random permutation of uranium atoms by dysprosium atom, the second is a systematic removal of oxygen atoms from the fluorite structure resulting in the ordered arrangement of uranium and dysprosium atoms, and the last one is a C-form rare earth oxide structure with random permutation of dysprosium atoms by uranium atoms. The behaviour of lattice parameter as a function of the dysprosium content can be explained if these three types of stoichiometric composition are assumed for the three regions of linear decrease observed in **Fig. 2**. This assumption seems particularly plausible in the fluorite-type solid solution, because the good agreement in the decreasing rate of lattice parameter between each group of specimens in the present study and KOSHCHEEV *et al.*'s implied the existence of a simple and basic structure. In this case, the region of constant lattice parameter is explained as non-stoichiometric composition $(U, Dy)O_{2-x}$. Introduction of cation interstitials would explain higher values of the lattice parameter than in stoichiometric composition $(U, Dy)O_2$. The invariance in lattice parameter is generally considered as indicating the appearance of the second phase. But in this case, the deviation from pseudo-binary condition enables the simultanious variation of Dy/U and O/(U+Dy) ratio so as to maintain the lattice parameter to a constant value. Therefore, it is not necessary to postulate the presence of the second phase. And moreover, the postulation of such a broad two-phase region seems to be inconsistent with the rapid transformation at room temperature observed in A-group specimens. The O/M ratio showed a rapid decrease at about 65%, and so the explanation is not an arbitrary one.

The ordered removal of oxygen atoms from fluorite structure and the ordered permutation of uranium and dysprosium atoms mean a f.c.c. to b.c.c. transformation accompanying a doubling of lattice parameter. Therefore, if this type of modification of fluorite structure is assumed for the single phase observed in the intermediate composition range, its similarity in X-ray diffraction pattern to the C-form phase may be understood. On the other hand, the rapid phase transformations at room temperature already described can also be explained, by considering the rapidness of order-disorder transformation. There is no definate evidence that this interemediate phase is an ordered structure of fluorite structure, and therefore further discussion on this phase would not be of much use. To make clear the nature of the phase transformation between this phase and fluorite-type solid solution, it will be necessary to carry out a thermal expansion measurement under rigorous control of the oxygen partial pressure.

# 5.  Conclusion

The ternary system U-Dy-O was studied approximately along the pseudobinary section $UO_2$-$Dy_2O_3$, and the followings were concluded.

1)  An intermediate phase exists at about 60 to 70 mole % of $DyO_{1.5}$. Its structure is

b.c.c. with lattice parameter about 10.8 Å. It is more stable at higher temperature and lower oxygen partial pressure.

2) Hypo-stoichiometric fluorite solid solution becomes more stable in an inert atmosphere with increasing of the dysprosium content, and this solid solution is associated with the intermediate phase through a phase transformation like order-disorder transformation.

3) Between the intermediate phase and C-form Dy$_2$O$_3$ phase, a broad two-phase region exists extending from about 70 to 90 mole % of DyO$_{1.5}$.

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