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Letter to the Editors

Study on solid solubility of Gd in UO_2 using X-ray diffraction

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Abstract

The change in solid solubility of Gd after sintering of UO_2 with Gd additions has been explained based on the X-ray diffraction study. It was observed that Gd has large solid solubility in UO_2 due to the same ionic radii of U^{4+} and Gd^{3+} in the lattice. On sintering, the observed reduction in the lattice parameter of UO_2 with Gd addition is due to formation of oxygen ion vacancies. Two different methods were used for the preparation of specimen materials: co-precipitation and mechanical mixing. The co-precipitation route, unlike mechanical mixing route, gives atomistic mixtures where lattice parameter changes before sintering with addition of Gd.

1. Introduction

Gd is used as a burnable poison in the enriched uranium dioxide pellets to get flux flattening in a BWR core. The normal quantity of Gd used is about 1.5 wt% in UO_2 pellets. Two routes have been developed for obtaining the UO_2–Gd_2O_3 mixtures. The manufacturing details using mechanical mixtures and co-precipitation routes are discussed by Balakrishna et al. [1]. In case of the mechanical mixing technique the oxide powders were mixed together and milled. While in the co-precipitation route a calculated quantity of gadolinium nitrate is mixed with uranly nitrate. The precipitate obtained by ammonia addition is dried, calcined and reduced to obtain UO_2–Gd_2O_3 co-precipitated powder mixture. In that investigation [1] it was concluded that densification during sintering for co-precipitated UO_2–Gd_2O_3 mixture powder was better than that for pure UO_2. It was proposed that this is due to decrease in anion diffusivity by cluster formation. In the present study, the focus is on the effect of the processing routes and Gd addition, on solid solubility of Gd in UO_2. The changes in the structure of UO_2 by addition of Gd can be correlated to the observed behaviour during sintering.

Wada et al. [2] have discussed the manufacturing experience of $UO_2 + Gd_2O_3$ fuel and determined lattice parameter as a function of Gd concentration. In the study by Momin et al. and Assmann et al. [3,4] no explanation was given for the observation that the lattice parameter decreases with increase in concentration of Gd. Thus the physical basis needs to be established for this decrease in lattice parameter after sintering. Moreover the effect of processing route on solubility of Gd in UO_2 is required to be investigated. Also the reason for high solubility of Gd in UO_2 needs to be established.

2. Experimental

UO_2 powder mixtures with various wt% of Gd were prepared to determine the effect of addition of Gd_2O_3 on crystal structure of UO_2. Samples with 2.5, 5.0, 7.5 and 10.0 wt% Gd were prepared using two different routes, i.e., by co-precipitation and by mechanical mixture. Samples from these routes were analysed by X-ray diffraction at two stages i.e., (a) pre-sintered powder, (b) sintered pellet powder. A scheme of sampling with identification is given in Table 1.

The X-ray diffraction data was obtained using Cu K_α with a curved crystal monochromator, the scan speed

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Table 1
Sampling scheme for experiment from two routes i.e., by mechanical mixture and co-precipitation

Route	Sampling stage	Wt % Gd			
		2.5	5.0	7.5	10.0
Mechanical mixture	Pre-sintered pellet powder	M-2.5 P	M-5 P	M-7.5 P	M-10 P
	Sintered pellet powder	M-2.5 PP	M-5 PP	M-7.5 PP	M-10 PP
Co-precipitated	Pre-sintered pellet powder	P-2.5 P	P-5 P	P-7.5 P	P-10 P

for precise lattice parameter measurement was 0.1°/min in the 2θ range 20–90°. Peak smoothing was carried out using Savitzkey–Golay's method [5], the background correction was done using Sonnevelt–Visser's method [6] and $K_{\alpha 2}$ stripping was done using $K_{\alpha 1}/K_{\alpha 2}$ ratio as 0.5.

2.1. Precise lattice parameter measurement

In order to study the effect of addition of Gd on the lattice parameter of UO_2, the precise lattice parameter were measured for the sintered powder for the two routes. Following procedure was used for the measurement. With this procedure it is possible to calculate the change in lattice parameter up to 0.0002 nm accurately.

(a) Diffractometer was precisely aligned with standard sample for accurate measurements.
(b) Very slow scan speed for high angle peaks (0.1°/min) was used.
(c) As there are very few peaks in the high angle 2θ range 'Nelson–Riley' method was used for the calculation of precise lattice parameter. With this method it is possible to use lower angle diffraction peaks for calculation. The following function of θ is plotted (on X-axis) against the lattice parameter (Y-axis) calculated at a given θ angle

$$\text{N–R function} = \cos^2\theta/\sin\theta + \cos^2\theta/\theta. \qquad (1)$$

(d) With this function the coefficient of correlation of fit for linear regression was high even if low angle peaks were included in the calculation. The precise lattice parameter is calculated by finding out the Y-intercept at $X = 0$ (i.e., when $\theta = 90°$ for N–R function).

3. Results and discussion

It is observed from Fig. 1 that for the mechanically mixed route, with increase in Gd concentration, there is significant change in lattice parameter for pre-sintered powder. In case of co-precipitation route there is decrease in lattice parameter with the increase of the concentration of Gd for the pre-sintered powder. It shows Gd in UO_2 is atomistically mixed when co-precipitation route is used as compared to mechanical mixture route.

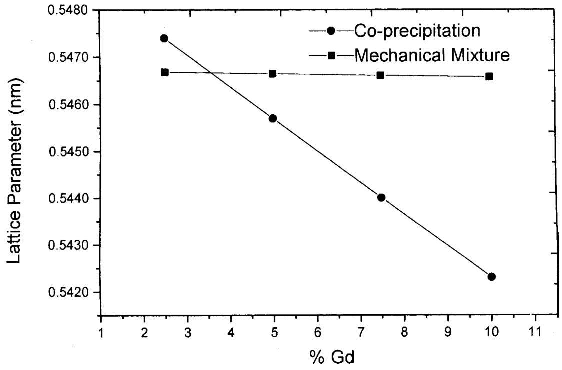

Fig. 1. Variation of lattice parameter of UO_2 with % Gd for powder samples before sintering.

Fig. 2 shows there is a decrease of lattice parameter after sintering in both the routes of powder production. It shows there is complete solid solubility of Gd in UO_2 after sintering, irrespective of the routes produced. It is observed that as the concentration of Gd is increased the lattice parameter decreases. Also the variation of the lattice parameter with Gd concentration is same for the two routes i.e., mechanically mixed and co-precipitated.

To summarize, the X-ray analysis of UO_2–Gd_2O_3 mixture (Gd upto 10 wt%) resulted in following conclusions:

(a) There is a large solid solubility of Gd in UO_2.
(b) The lattice parameter of UO_2 decreases with addition of Gd.
(c) The processing route of the powder has no effect on the solubility of Gd in UO_2 after sintering.

These results can be explained as follows:

In the lattice, Gd^{3+} and U^{4+} radii changes with coordination number (CN) as given in Table 2. UO_2 structure is fluorite structure (anion at simple cubic arrangement and alternate cubic body centers occupied by cations). U (present as 4+) has CN = 8. Hence in UO_2, U^{4+} has ionic radii of 114.0 in UO_2 crystal structure.

When one Gd^{3+} replaces U^{4+} UO_2, it leads to 1 number $V_O^{\bullet}$ (oxygen ion vacancy) as Gd is present as

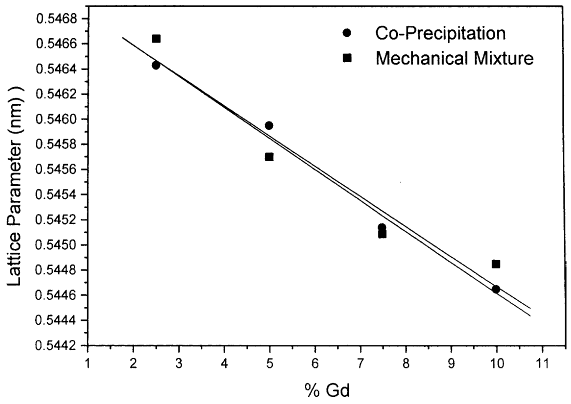

Fig. 2. Variation of lattice parameter of UO_2 with % Gd for powder samples after sintering.

Table 2
Ionic radii of Gd^{3+} and U^{4+} with change in CN [6]

CN	Ionic radii (pm)	
	Gd^{3+}	U^{4+}
6	107.8	103.0
7	114.0	109.0
8	119.3	114.0
9	124.7	119.0
12	–	131.0

Gd^{3+} i.e., for each atom of Gd one $V_{\mathrm{O}}^{\bullet}$ is created [7]. Gd^{3+} when present in UO_2 lattice is associated with 7 U^{4+} ions and one $V_{\mathrm{O}}^{\bullet}$. Hence Gd^{3+} will have CN as 7. Thus the ionic radii of Gd^{3+} in UO_2 lattice will be 114.0. As the ionic radii of the dopant (Gd^{3+}) matches perfectly with the parent atom (U^{4+}) the dopant will exhibit unlimited solid solubility in UO_2.

Creation of 1 $V_{\mathrm{O}}^{\bullet}$ by replacement of one U^{4+} by Gd^{3+} will result in shrinkage in the lattice. Thus as the Gd concentration increase the lattice parameter should decrease.

During the co-precipitation process the Gd atoms are atomically mixed in the process and hence with change in the concentration of Gd the lattice parameter changes in the powder stage. While in case of the mechanical mixture route the atomic mixing does not takes place, but during sintering the Gd atoms replace U atoms and there is change in the lattice parameter only after sintering.

In case of other fluorite structures oxides like zirconia a phase transformation from monoclinic to tetragonal is observed. On doping with yttria stabilization of high temperature tetragonal phase takes place. This behaviour can be explained by considering the changes in the lattice with doping. Zr^{4+} has CN as 8 in ZrO_2 lattice with ionic radii as 98 when Y^{3+} replaces Zr^{4+} it has CN 7 and ionic radii 110 (Table 3). There is a lattice strain (expansion) with addition of Y^{3+}. Thus above 4 mol% Y addition stabilizes tetragonal phase [9].

Table 3
Ionic radii of Y^{3+} and Zr^{4+} with change in CN [8]

CN	Ionic radii (pm)	
	Y^{3+}	Zr^{4+}
6	104	86
7	110	92
8	116	98
9	122	103

4. Conclusions

1. Gd_2O_3 is present as a solid solution in UO_2 after sintering in the concentration investigated (i.e., upto 10%).
2. There is a perfect match of ionic radii of dopant and matrix thus there is high solid solubility. No free Gd is present.
3. With increase in concentration of Gd the lattice parameter of UO_2 decreases. This has been explained due to formation of oxygen ion vacancies by addition of Gd, which leads to shrinkage of the lattice.
4. The lattice parameter for the mechanically mixed powder and the co-precipitated powder is similar after sintering. They decrease identically with increase in Gd concentration. Thus the powder preparation routes selected here have no influence on the lattice parameter of the mixture after sintering.

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