Measurement of Gd content in (U,Gd)O$_2$ using thermal gravimetric analysis

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Abstract

We propose a simple and precise method for measuring the Gd content in the (U,Gd)O$_2$ pellet by only measuring the weight variation of the pellet during thermal heat treatment in air. The (U,Gd)O$_2$ fuel pellets were oxidized at 475 °C, subsequently heat treated at 1300 °C, and then cooled to room temperature in air. The accompanying weight variations were measured using thermo gravimetric analysis (TGA). The measured weight variations were mathematically analyzed with reference to the successive phase reactions during the heat treatment. This method provides an advantage in that the rare-earth element content including Gd can be measured using relatively simple equipment such as an electric furnace and a balance.
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1. Introduction

Nuclear reactors use UO$_2$ as a nuclear fuel material. A mixture of UO$_2$ and neutron absorbing materials is used to control the nuclear fission in nuclear reactors, together with UO$_2$ fuel [1–3]. Lanthanides (hereinafter referred to as 'Ln') such as Gd(Gadolinium), Er(Erbium), Eu(Europium) and Sm(Samarium) may be used as neutron absorbing materials. Among these, Gd is the most commonly used. The nuclear fuels containing such lanthanides are referred to as burnable absorber fuels.

The Ln content dissolved in the (U,Ln)O$_2$ nuclear fuel should be measured precisely since it greatly affects the nuclear fission behavior. In general, the Ln content of the (U,Ln)O$_2$ nuclear fuel is usually measured using an energy dispersive X-ray spectrometry or an inductive coupled plasma mass spectrometry.

Phase relationships between lanthanide oxide and uranium oxide have been investigated in high oxygen partial pressures by several researchers [4–9]. They found that the solubility of the lanthanide elements in UO$_{2+x}$ decreased by increasing x, and that the solubility of lanthanide elements in the U$_3$O$_8$ phase was below the 0.5 mol%.

The non-equilibrium and unstable (U,Ln)$_3$O$_8$ solid solution can be obtained by applying special processing conditions. Taylor and Mceachern [9] and You et al. [10] have found that an unstable (U,Ln)$_3$O$_8$-type phase can be formed by the oxidation of (U,Ln)O$_2$ above 350 °C. However, the (U,Ln)$_3$O$_8$-type phase is so unstable as to be readily separated into a Ln-rich fluorite phase and a U$_3$O$_8$ phase by a heat treatment above 950 °C [9,11].

In this work, we investigate the accompanying weight variation when the (U,Gd)O$_2$ fuel pellet is oxidized and

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* Corresponding author. Address: Advanced LWR Fuel Development, Korea Atomic Energy Research Institute, 150 Dukjin-dong, Yuseong-gu, Daejon 305-600, South Korea. Tel.: +82-42 868 2556; fax: +82-42 861 7340.
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heat treated in air. The measured values were mathematically analyzed with reference to the successive phase reactions during the oxidation and heat treatment. As a consequence, the Gd content in the $(U,Gd)O_2$ pellet can be simply and precisely measured by only measuring the weight variation of the pellet during thermal heat treatment in air.

2. Experimentals

$(U,Gd)O_2$ nuclear fuel pellets whose Gd contents, Gd/(U + Gd), are 2.951%, 5.846%, 8.685% and 14.205% respectively, were prepared. Each powder mixture of UO_2 and Gd_2O_3 was wet ball-milled, pressed into cylindrical pellets and sintered in H_2 at 1720 °C for 4 h. The sintered pellets were held at 1650 °C for 20 h in a gas mixture of CO_2 and H_2 ($CO_2/H_2 = 0.3$) for the purpose of chemical homogenization. And then the annealed sample pellets were cooled to room temperature in 3% CO_2 containing H_2. The cooling rate was 4 K/min. The formation of single-phase solid solution was characterized by using X-ray diffraction and EPMA area mapping.

The three step heat treatments were subsequently applied to each sample. First, the sample was rapidly heated to 475 °C in air and then held for 4 h. In the second step, the sample was subsequently heated in air at a rate of 10 K/min and was maintained at 1300 °C for 4 h. Finally, the sample was cooled to room temperature in air at a rate of 4 K/min. The weight changes during the heat treatment were monitored by TGA (Shimadzu, TG-50).

The morphology and cation concentration profiles were investigated by SEM and EPMA (Camebax SXR).

3. Results and discussion

The formation of single-phase solid solution samples was confirmed by the X-ray diffraction and EPMA area mapping. The X-ray diffraction patterns of samples showed single-phase diffractions with the narrow and sharp diffraction lines. The EPMA area-mapping contours also showed no significant composition variation in 500 μm × 500 μm sample region.

3.1. Phase reaction equation

Fig. 1 shows a typical feature of the weight variation occurring during the subsequent three step heat treatment for $(U,Gd)O_{2+x}$. The initial composition and weight were $(U_{0.913}Gd_{0.087})O_{2.00}$ and 684 mg, respectively. The dotted line indicates the temperature change, and the solid line indicates the weight change. In the ramping and holding at 475 °C, the weight of the sample increases rapidly and then remains constant. In the heating from 475–1300 °C, the sample weight starts to decrease, and the weight loss accelerates at about 1000 °C. In the holding at 1300 °C, the sample weight decreases gradually and then remains constant. In the cooling to room temperature, the sample weight increases considerably.

The phase reactions occurring during the thermal treatment can be divided into three reactions according to the annealing temperature step and corresponding saturated weight (denoted in Fig. 1).
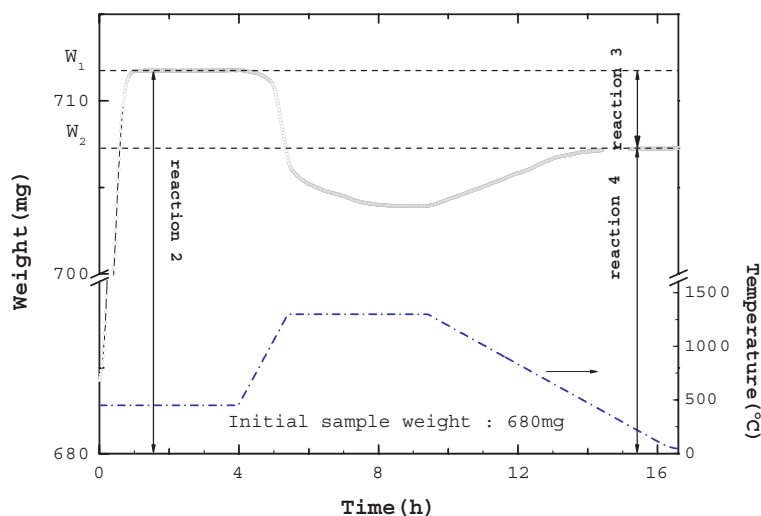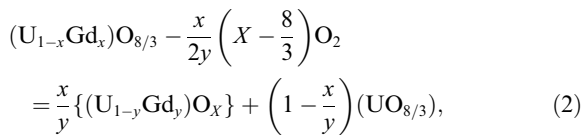

Fig. 1. Typical weight change during the oxidation and subsequent heat treatment of $(U_{0.913}Gd_{0.087})O_2$.

The initial composition of a certain Gd-dissolved UO_2 sample is described as $(U_{1-x}Gd_x)O_{2+z}$. Here, x is the initial Gd content of $(U,Gd)O_2$, and z is the value when the O/(U + Gd) ratio of the initial sample is higher than 2.0. $(U_{1-x}Gd_x)O_{2+z}$ is oxidized from the UO_2-type cubic phase to the U_3O_8-type orthorhombic phase during the first heat treatment step [9–11] according to reaction

$$(U_{1-x}Gd_x)O_{2+z} + \frac{1}{3}O_2 - \frac{z}{2}O_2 = (U_{1-x}Gd_x)O_{8/3}. \qquad (1)$$
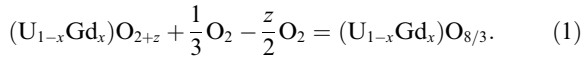
The oxidized $(U,Gd)_3O_8$ phase is separated into the Gd-enriched fluorite phase and the Gd-free U_3O_8 type phase during the following second heat treatment step [9,11]. The weight might be decreased because part of the $(U,Gd)_3O_8$ type phase is reduced to the fluorite phase. The weight reduction is saturated after the phase separation is completed.

The weight of the sample is increased during the last cooling step to room temperature. The equilibrium oxygen to metal ratios of both phases are smaller at a high temperature than at a low temperature [12–14]. So, the sample weight is increased as the temperature is decreased. The room temperature stoichiometry of the Gd-free phase should be U_3O_8, if the cooling rate is sufficiently slow so that an equilibrium composition is achieved. Then the phase separation *reaction* 3 in Fig. 1 could be expressed as

$$(U_{1-x}Gd_x)O_{8/3} - \frac{x}{2y}\left(X - \frac{8}{3}\right)O_2$$
$$= \frac{x}{y}\{(U_{1-y}Gd_y)O_X\} + \left(1 - \frac{x}{y}\right)(UO_{8/3}), \qquad (2)$$

where y and X are the Gd and oxygen composition of the separated fluorite phase, respectively.

3.2. Determination of the Gd cation composition from the weight change

We have defined W_1 and W_2 as the saturated sample weight at the first heat treatment step and saturated sample weight at the final heat treatment step, respectively. The weight difference between W_2 and W_1 is the mass of the discharged oxygen gas in Eq. (2). Then, $(W_1 - W_2)/W_1$ can be obtained from the Eq. (2) as follows:

$$\frac{W_1 - W_2}{W_1} = \frac{MW_{O_2}\left(\frac{x}{2y}\left(-X + \frac{8}{3}\right)\right)}{MW_{(U_{1-x}Gd_x)O_{8/3}}}$$
$$= \frac{15.9994 \cdot x \cdot (-X + 2.667)}{y \cdot (280.70 - 80.78 \cdot x)}, \qquad (3)$$

where MW_{O_2} is the O_2 molecular weight, $MW_{(U_{1-x}Gd_x)O_{8/3}}$ is the $(U_{1-x}Gd_x)O_{8/3}$ molecular weight, x is the Gd content dissolved in $(U_{1+x}Gd_x)O_{2+X}$, X is the oxygen to metal ratio in the separated fluorite phase and y is the Gd cation content dissolved in the separated fluorite phase.

The $(W_1 - W_2)/W_1$ can be calculated from the W_1 and W_2 measured from the TGA experiment. Therefore, if y and X at a fixed thermal treatment condition are determined, we can calculate the unknown initial Gd content dissolved in $(U,Gd)O_2$ by conducting a thermal treatment in the same condition and measuring W_1 and W_2. Eq. (3) is a function not related to the weight of the initial sample, so the Gd content can be determined without the information from the O/(U + Gd) ratio of an initial sample.

A series of known contents for the Gd dissolving $(U,Gd)O_2$ samples were prepared. The O/(U + Gd) ratio of each sample was 2.00. The three step heat treatments were applied to each sample. The W_0 (initial sample weight), W_1, W_2 value of the samples and the weight variation $(W_1 - W_2)/W_1$ (%) calculated from these values are summarized in Table 1. Fig. 2 shows the Gd mole fraction vs. $(W_1 - W_2)/W_1$ graph.

The Gd content in the separated fluorite phase at room temperature was determined by EPMA. The Gd composition was slightly varied with the measured points or samples. However, the variation was small and shows no dependency on the initial Gd content. The average Gd mole fraction in the Gd-enriched region was 0.33. The experimental determination of X was not attempted because the sampling of a sole fluorite phase from the mixture of U_3O_8 and the fluorite phase is difficult. However, the oxygen composition X in a separated fluorite phase can be numerically determined by fitting the measured values in Fig. 2 with Eq. (3) using the least square method. The result showed that X was

Table 1
The measured weight variations during the thermal treatment of $(U,Gd)O_2$

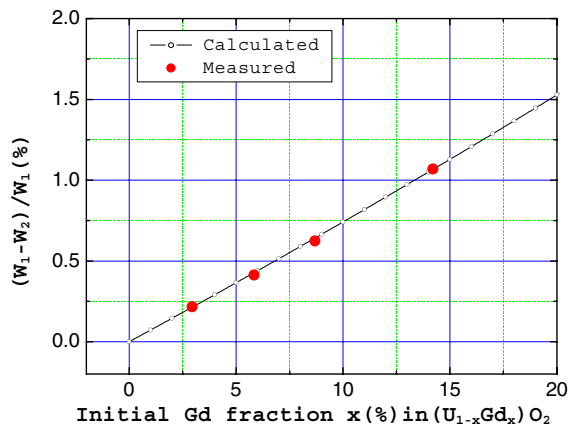| Gd_2O_3 weight fraction in UO_2–Gd_2O_3 (%)	Gd mole fraction in $(U,Gd)O_2$ (%)	W_0 (mg)	W_1 (mg)	W_2 (mg)	$(W_1 - W_2)/W_1$ (%)
2	2.951	635.4	660.64	659.22	0.2149
4	5.846	607.3	631.64	629.04	0.4116
6	8.685	684.0	711.72	707.31	0.6196
10	14.205	830.5	864.46	855.32	1.0573

Fig. 2. The relationship between the weight ratio of $(W_1 - W_2)/W_1$ and the initial mole fraction of Gd in $(U,Gd)O_2$. The calculated value using Eq. (4) and the measured value of $(W_1 - W_2)/W_1$ coincide well with each other.

2.253(2). The numbers in parentheses mean the estimated standard deviations. The obtained value of X by fitting seems to have a reasonable physical meaning. The oxygen composition of 2.253 is very close to the O/M ratio of the U_4O_9 phase. The U_4O_9 phase has the highest oxygen composition among the cubic fluorite phases [15,16]. It is expected that the oxygen composition of the separated cubic phase, which was reduced in air, might be very similar to that of the U_4O_9 phase. So, we define X as 9/4 in this work.

By adopting the determined X value to Eq. (3), Eq. (3) can be simplified even further as

$$\frac{W_1 - W_2}{W_1} = \frac{159.994 \cdot x}{24 \cdot y \cdot (280.70 - 80.78x)}. \tag{4}$$

The calculated $(W_1 - W_2)/W_1$ obtained from Eq. (4) is plotted in Fig. 2 for a comparison with the measured $(W_1 - W_2)/W_1$. It can be found that the calculated values using Eq. (4) are in good agreement with the measured values. The Gd content of the $(U_{1-x}Gd_x)O_{2+z}$ nuclear fuel pellet can be precisely measured using Eq. (4) by only measuring the weight variation during heat treatment in air.

Because the Gd cation composition in the separated phase and, consequently, the oxygen stoichiometry depend on the thermal treatment conditions, the experiment should be carried out at a fixed thermal treatment condition.

In this work, we introduce a method for measuring the initial Gd contents in a $(U,Gd)O_2$ system using the TGA method. This method can be promisingly extended to the measurement of the contents of lanthanide elements, because the phase separation during heat treat-

ment in air is a common phenomena in lanthanide-dissolved $(U,Ln)O_2$ [9].

4. Conclusion

A method of determining the Gd content of $(U,Gd)O_2$ fuel has been developed which only needs two different weight measurements during thermal treatment and a simple calculation of the correlation with the weights. The thermal treatment includes oxidizing $(U,Gd)O_2$ to $(U,Gd)_3O_8$ in air and annealing the $(U,Gd)_3O_8$ at 1300 °C in air and then cooling it to produce $(U,Gd)O_{2.25}$ and U_3O_8.

The phase reactions involved in the thermal treatment can be described using the mass balance equations. The equations suggest that the Gd content is a simple correlation of weight change with the experimental constants. The Gd contents of $(U,Gd)O_2$ fuels containing Gd up to 14 at.% are in very good agreement with those determined by the developed method.

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