Solubility of Gd in UO$_{2\pm x}$

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1. Introduction

Binary oxide system of UO$_2$-Gd$_2$O$_3$ is one of the typical burnable absorbers. Natural Gd has a large neutron absorption cross-section and can control the reactivity of reactor core by absorbing excess neutrons in the early stage of fuel operation. In addition, since the secondary isotopes of Gd show low cross-section, it can minimize the reactivity penalty at end-of-cycle.

Recently, the efforts are underway in nuclear industry to increase uranium enrichment higher than 5% to achieve long-fuel cycle length and reduce the spent fuels. In addition, the soluble boron-free core is a major design requirement for advanced light water reactors such as SMR. Accordingly, the total amount of Gd introduced into nuclear fuel and/or core is expected to increase further. To evaluate the fuel performance of the UO$_2$-Gd$_2$O$_3$ system with high content of Gd, it would be necessary to understand the phase equilibrium between UO$_2$ and Gd$_2$O$_3$ including solubility between the two oxide components and corresponding crystal structure changes.

In this study, we re-evaluate the solubility limit of Gd in the UO$_2$ lattice of the fluorite structure and compared with literature. The nonlinear reduction of lattice constant was discussed in terms of the charge balance between oxidized U and Gd cations.

2. Experimental

The sample powders were prepared by mixing weighted quantities of UO$_2$ and Gd$_2$O$_3$ for 2h in a planetary mill. The powder mixtures were heat treated at 1400°C for 20h under Ar-4%H$_2$ atmosphere. After calcination, the powders were milled again for 2h in a planetary mill. The sintered pellets were fabricated by sintering the green pellets at 1700°C for 6h under dry H$_2$ gas atmosphere. After sintering, the weight gain of a selected sample during the annealing in high temperature air were measured using TGA. Phase analysis of the sintered particles was performed using XRD (Rigaku Ultima IV) with Cu-K αradiation operated at 40 kV and 30 mA.

3. Results

Fig. 1 shows the XRD patterns of samples sintered in reducing atmosphere. The patterns reveal that Gd is soluble in fluorite structure up to 66.7 mol%.
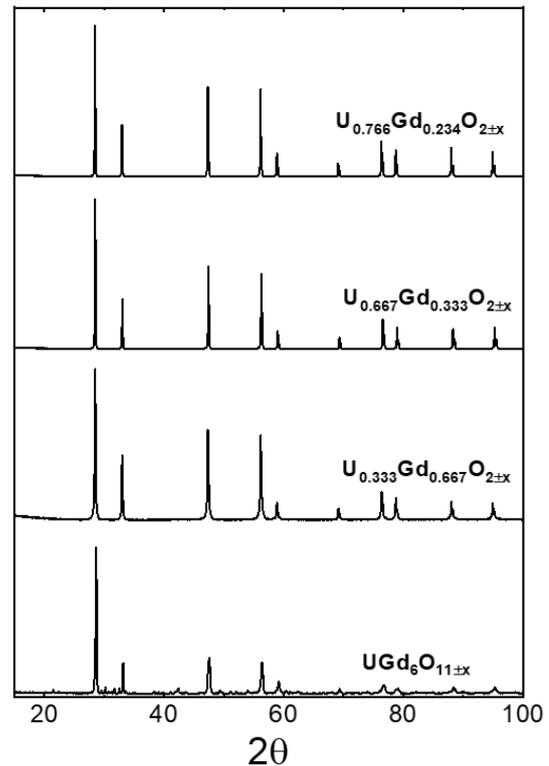
Fig. 1. XRD patterns of sintered pellets

The sintered sample of U$_{0.333}$Gd$_{0.667}$O$_{2\pm x}$ was selected and the weight gain during the oxidative annealing under 1200°C of air was measured by using TGA. About 1.3% of weight gain (Fig. 2(a)) indicated that the sample was oxidized during the annealing. The XRD pattern (Fig. 2(b)) also shows the increase of lattice constant after the annealing.

Using XRD patterns in Fig. 1, the lattice constants of solid solutions were calculated and compared with the values of the literature (Fig. 3). The calculated lattice constants of this work agree well with the literature values.

The two dash-lines in Fig. 3 are lattice parameter of U$_{1-y}$Gd$_y$O$_{2.00}$ type solid solutions as a function of Gd concentration, y. Since the O/M ratio is fixed to be 2.00, when Gd^{3+} is substituted for U^{4+} in the cation lattice, some of the remaining U^{4+} atoms should be oxidized to

U^{5+} or U^{6+} in order to fulfill the charge balance (electrical neutrality). Assuming that U^{4+} is oxidized to U^{5+}, the number of U^{4+} cations decrease faster with Gd contents due to the charge compensation rule. The ionic radius of Gd^{3+} is slightly larger than that of U^{4+}. On the other hand, the ionic radius of U^{5+} and U^{6+} is smaller than that of U^{4+}. Therefore, the slop of lattice constant is more negative for U^{5+} case (black dash-line) than for U^{6+} case (red-dash line).

(a)   (b)
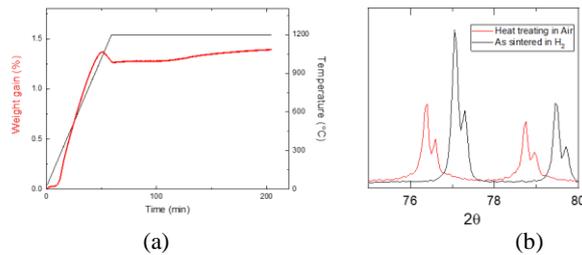
Fig. 2. (a) Weigh gain during the annealing at high temperature of air. (b) Comparison of XRD patterns after the annealing
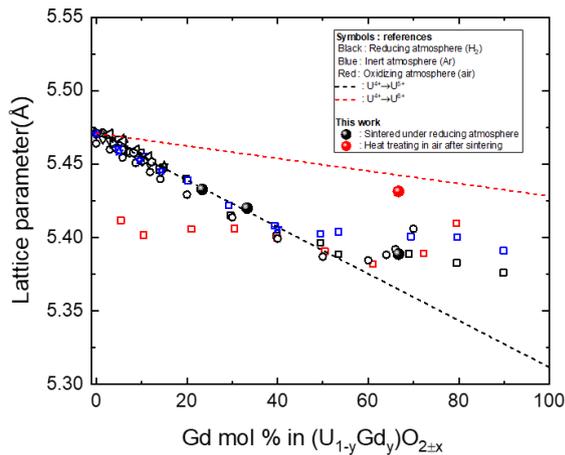
Fig. 3. Summary of lattice parameters in $U_{1-y}Gd_yO_{2\pm x}$ system together with experimental results of this work. [1-5]

In the range of y from 0 to ~0.5, experimental results follow the black dash-line, which indicates that U^{5+} exists in preference to U^{6+} up to about 50mol% of Gd. However, if the y is increased further, the experimental results start to deviate from the linear curve. At y=0.5, the chemical form of the solid solution is described as $U^{5+}_{0.5}Gd^{3+}_{0.5}O^{2-}_{2.00}$. At this composition, all U^{4+} cation is exhausted. Therefore, it is obvious that if y exceeds 0.5, corresponding amount of U^{5+} must be oxidized to U^{6+} to maintain O/M ratio of 2.00 and consequently, the lattice constant must deviate from the black line. Considering the ionic radius of cations, size of oxygen vacancy and the variation of coordination number, if y exceeds 0.5, the lattice parameters is expected to be located between the black and red dash-lines and Fig. 3 shows a good agreement with the expectation.

The XRD patterns in Fig.1 and Fig.2 (b) confirm that $U_{0.333}Gd_{0.667}O_{2.00\pm z}$ is a single phase solid solution. If the O/M ratio of this compound is 2.00, all U cation should be U^{6+} and the lattice constant of this solid solution would follow the red-dash line in Fig. 3. The lattice constant of the sample annealed in air is close to the red line as shown in Fig. 3, which is indicating the possibility that the U^{6+} is a dominant cation in this case.

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