The Relationship between Oxygen Composition and Lattice parameter in a UO₂-Gd₂O₃ System with High Gd₂O₃ Content

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1. Introduction

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 UO₂-Gd₂O₃ system with high content of Gd, it would be necessary to understand the phase equilibrium between UO₂ and Gd₂O₃ including relationship between the oxygen composition and corresponding unit-cell lattice parameter.

In this study, the change of lattice constant in UO₂-Gd₂O₃ system with variation of oxygen composition wase discussed in terms of the charge balance between oxidized U and Gd cations, and the formation of oxygen vacancies as well. The experimental and theoretical findings will serve as a foundation for understanding changes in lattice constants, O/M ratio, and re-sintering density for high-Gd content burnable absorber pellets.

2. Experimental

The sample of $U_{0.333}Gd_{0.667}O_{2\pm x}$ was selected. The sample powders were prepared by mixing weighted quantities of UO₂ and Gd₂O₃ for 2h in a planetary mill. The powder mixture was heat-treated at 1400°C for 20h under Ar-4%H₂ atmosphere. After calcination, the powder was milled again for 2h in a planetary mill. The sintered pellets were fabricated by sintering the green pellets at 1700°C for 6h under wet H₂ gas atmosphere.

After sintering, the pellet was annealed in high temperature air and dry H₂. The weight gain of the sample pellet during the annealing was monitored using TGA. Phase analysis of the samples after the annealing was performed using XRD (Rigaku Ultima IV) with Cu-K αradiation operated at 40 kV and 30 mA.

3. Results

Fig. 1 shows the lattice parameter change of sample pellet according to the annealing condition [1-11]. The lattice parameters were obtained by using the X-ray diffraction patterns. It is expected that the sample annealed in air has the highest oxygen to metal (O/M) ratio and the sample annealed in dry H₂ will have the smallest O/M ratio. Therefore, Fig. 1 indicates that the lattice parameter of sample pellet decreases with increasing O/M ratio.
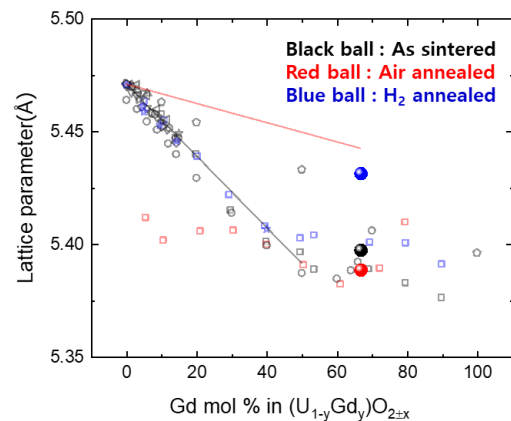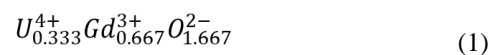

Fig. 1. Lattice parameter variation depending on annealing

If the oxygen potential is low enough for all uranium cations to exist as U⁴⁺, the electrical neutrality of the sample can be maintained through the formation of oxygen vacancies. The composition of the specimen can then be described by Equation 1.

$$U_{0.333}^{4+}Gd_{0.667}^{3+}O_{1.667}^{2-} \tag{1}$$

Conversely, if the oxygen potential is sufficiently high for all uranium cations to exist as U⁶⁺, then the composition of the specimen that satisfies electrical neutrality can be represented by Equation 2.

$$U_{0.333}^{6+}Gd_{0.667}^{3+}O_{2.0}^{2-} \tag{2}$$

If the oxygen potential is very low, uranium cations exist as U⁴⁺, and to fulfill electrical neutrality, an equivalent amount of oxygen vacancies is created.

As the oxygen partial pressure increases, U⁴⁺ is preferentially oxidized to U⁵⁺, and when U⁴⁺ is depleted, U⁵⁺ is oxidized to U⁶⁺. Knowing the equilibrium composition of U cations automatically determines the oxygen composition that satisfies electrical neutrality. Then, we can calculate the lattice parameter by using the compositions of cations, oxygen, and oxygen

vacancies along with information on the ionic radius. In this system, various types of uranium ions exist depending on the oxygen potential, and the concentration of oxygen vacancies is also high. Therefore, it is anticipated to have a locally very complex structure. Consequently, to determine the lattice constant, we must consider not only the composition but also the change in coordination number and the information regarding ionic radii.

Pauling's rule predicts the ionic radius that enables a stable lattice structure of ionic compounds. Since the ionic radius of uranium decreases with increasing oxidation state, the radius of the oxygen combined with uranium cation should decrease to satisfy Pauling's rule.

Figure 2 shows the calculated lattice constants of specimens with compositions given by Eq.1 and 2, assuming that the oxygen ion radius is 1.356Å. The results confirm that the increase in the lattice constant, corresponding to the decrease in the O/M ratio, can be theoretically calculated by considering the oxidation of uranium cation and the generation of oxygen vacancies.
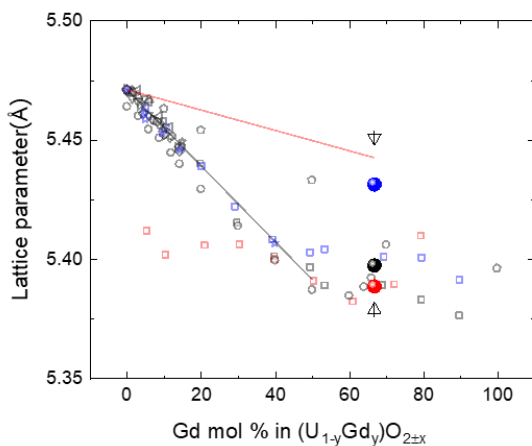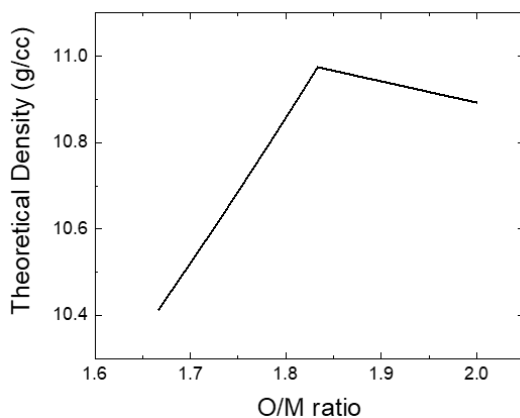

Fig. 2. Calculated lattice parameters

Fig. 2. Calculated theoretical density

Fig. 3 illustrates the variation in theoretical density values according to the O/M ratio, calculated from

lattice constants shown in Fig. 2. As depicted in the figure, the theoretical density may vary depending on the manufacturing or heat treatment conditions of the specimen, even if the cation composition remains the same. Therefore, to accurately measure the relative density of the manufactured specimens, it is essential to provide the O/M ratio values corresponding to the manufacturing conditions.

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