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High-temperature reaction of (U, Gd)O_2 with zirconium

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Abstract

The reaction between (U, Gd)O_2 and Zr was examined to elucidate the effect of Gd on the reaction kinetics and morphology. The (U, Gd)O_2 pellets with Gd_2O_3 contents from 1–8 wt% (8 mm ∅ × 2.5 mm) and Zr disks (8 mm ∅ × 5 mm) were used as specimens. The reaction between (U, Gd)O_2 and Zr was carried out in the temperature range of 1100–1400°C for 2–50 h in a vacuum below 10^{-5} Pa. The heating and cooling rates were kept 5°C/s. The UO_2/Zr reaction produced typically three layers: αZr(O) + (U, Zr), (U, Zr) and αZr(O). For the (U, Gd)O_2/Zr reaction, the morphology of the reaction layers was slightly different from that of the UO_2/Zr reaction. The reaction was found to follow the parabolic rate law. The layer growth rate constants and the activation energy for the reaction were estimated from the experimental data. Below a temperature of 1200°C, the growth rate constants were smaller for (U, Gd)O_2/Zr than for UO_2/Zr. The activation energy for the layer growth was larger for (U, Gd)O_2/Zr than for UO_2/Zr.

1. Introduction

A considerable effort is being devoted for many years to the studies on the high temperature interaction of UO_2 fuel with zircaloy cladding to understand degradation of fuel and cladding under accident conditions of light water reactors [1–11]. In our previous studies, the phase diagram of U–Zr–O ternary system [12–14] and UO_2/Zr interfacial reaction [15,16] have been examined to obtain an exact knowledge of fuel-cladding interaction at elevated temperatures.

In light water reactors, gadolina has been widely employed as a burnable absorber to provide a negative moderator coefficient at the beginning of reactor life and help shape core power distributions. In recent years, higher gadolinia contents in UO_2 fuel have been required to attain extended burnup of fuel. The gadolinia addition is known to affect such thermal properties of UO_2 fuel as heat capacity, oxygen potential and thermal conductivity.

Although the interaction between UO_2 fuel and zircaloy cladding has been extensively studied from safety point of view, there is little information about high-temperature reaction of gadolinia-doped UO_2 fuel with cladding. In the present study, the high-temperature reaction between (U, Gd)O_2 and Zr has been therefore examined to elucidate the effect of gadolinia on the reaction kinetics of fuel-cladding interaction and the morphology of interfacial reaction zone.

2. Experimental

The specimens used in the present study were a zirconium disk (8 mm ∅ × 5 mm, 99.9% in purity) and a (U, Gd)O_2 pellet (8 mm ∅ × 2.5 mm, reactor grade). The Gd_2O_3 contents of (U, Gd)O_2 pellets were 1, 2, 4, 6 and 8 wt%. The reaction couple consisted of the zirconium disk sandwiched by the (U, Gd)O_2 pellets. The reaction couple was first degassed at 700°C for several hours in a vacuum below 10^{-5} Pa and then heated at 5°C/s up to the desired reaction temperature. Reaction experiments were performed at a temperature of 1100–1400°C for reaction time for 2 to 50 h and subsequently the couple was cooled at 5°C/s to room temperature. After the reaction experiments, the microstructure of reaction layer formed in the specimen was examined by optical and scanning electron

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microscopes and the interfacial reaction products were identified by an energy dispersive X-ray analyzer (EDXA).

3. Results and discussion

Fig. 1(a) shows the reaction layer formed between the UO_2 pellet and the Zr disk at a temperature of 1300°C for 0.25 h, together with a schematic illustration of the reaction layer. As can be seen in Fig. 1, three zones are found to be formed in the reaction layer: zone I; $\alpha Zr(O) + (U, Zr)$, zone II; (U, Zr), zone III; $\alpha Zr(O)$ [4–7,12,13]. This result for the morphology of UO_2/Zr reaction layer is in good agreement with the literature data for UO_2/zircaloy reaction [1–6]. The phase diagram of the U–Zr–O ternary system [7,8,13] suggests that metallic phases composed of uranium, zirconium and oxygen are hcp $\alpha Zr(O)$ solid solution and bcc (γU, βZr) solid solution. In the $\alpha Zr(O)$ solid solution phase, the uranium concentration is small and in the (γU, βZr) solid solution phase, the oxygen concentration is small.

The zone I consists of two phases: $\alpha Zr(O) + (U, Zr)$. In this zone, $\alpha Zr(O)$ shows a typical columnar structures. The (U, Zr) solid solution occupies only a few percent in volume fraction and the rest is occupied by the $\alpha Zr(O)$ [5,12]. The (U, Zr) solid solution is present as stringers along the grain boundaries of $\alpha Zr(O)$ and as globules inside the grains of $\alpha Zr(O)$. The zirconium concentration of the (U, Zr) is generally below 10 wt% and the oxygen concentration is less than 1 wt%. The original interface of UO_2/Zr determined by tungsten marker experiments lies between zone I and zone II. Therefore, the zone I is the zone produced in the original UO_2 region.

The zone II is the single phase zone composed of binary (U, Zr) solid solution and contains only a little oxygen. The morphology of zone II depended decisively

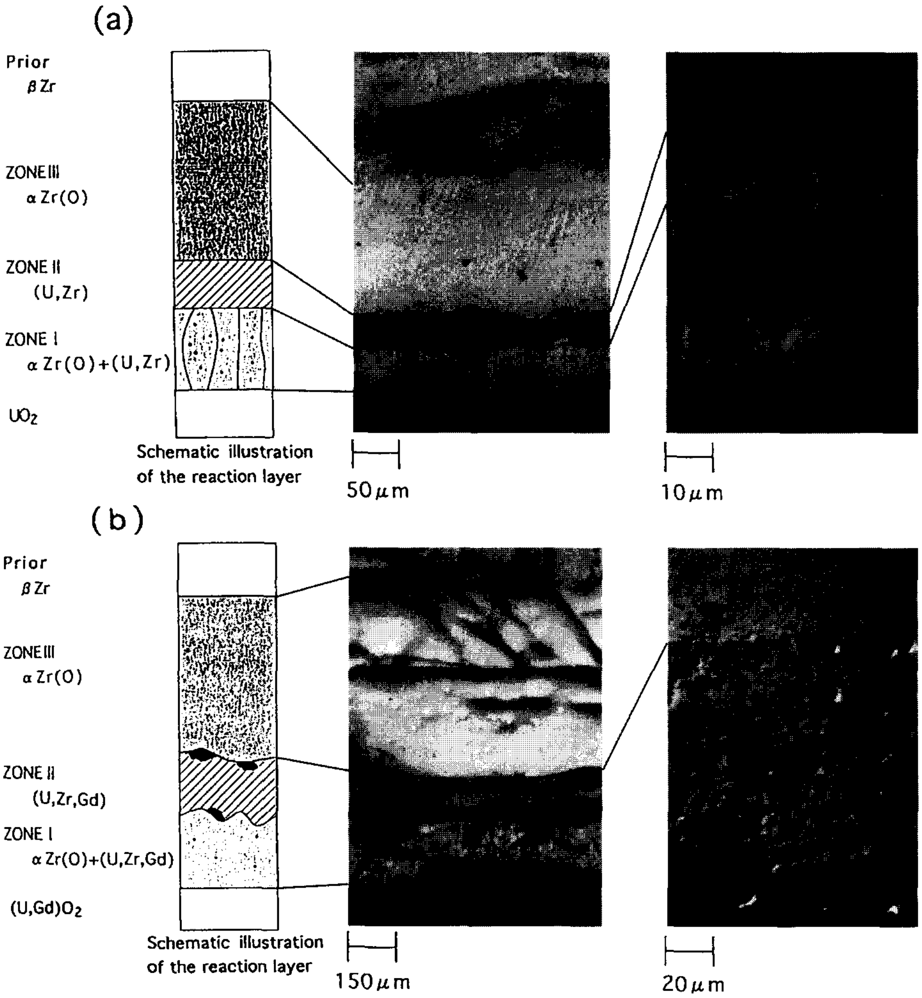

Fig. 1. The microstructures of UO_2/Zr and $(U, Gd)O_2/Zr$ reactions. (a) UO_2/Zr at 1300°C for 0.25 h. (b) $(U, Gd)O_2/Zr$ with the gadolinia content of 4 wt% at 1400°C for 2 h.

on temperature. The zone II formed at a low temperature has thorns toward zone III. The size and the number of thorns depended on the reaction time. At temperatures above 1300°C, zone II has no thorn and the interface between zone II and zone III were found to be flat. This may be related to the formation of liquid phase, the changes in the creep strength of reaction zones, or the differences in diffusion mechanism between the reaction temperatures.

The zone III is the layer composed of αZr(O) phase and has no uranium. Since oxygen diffuses from UO_2, the oxygen concentration of αZr(O) is larger in this zone than in zone II. The thickness of this zone is the largest among the reaction zones, irrespective of temperature or reaction time.

Fig. 1(b) indicates the micrograph of the reaction layer formed between (U, Gd)O_2 pellet with the Gd_2O_3 content of 4 wt% and Zr at a temperature of 1400°C for the reaction time of 2 h. In general, the number of the reaction zones and their sequence observed for (U, Gd)O_2/Zr reaction were almost the same as UO_2/Zr reaction. It is found from Fig. 1(b) that three reaction zones are formed between (U, Gd)O_2 and prior βZr. The morphology of the (U, Gd)O_2/Zr reaction zones slightly differs from that of UO_2/Zr reaction zones. Since there exists no information about the phase diagram of U–Zr–Gd–O quaternary system, the phases formed in the reaction zone cannot be predicted by the phase diagram.

Zone I appears to consist of mainly two phases: αZr(O) + (U, Zr, Gd). The results for the EDXA analysis indicated that the αZr(O) in this zone contained a small amount of gadolinium and that the gadolinium concentration of the (U, Zr, Gd) solid solution phase was small. In this zone, small UO_2 globules and precipitates with high concentration gadolinium were often observed by the EDXA analysis. The (U, Zr) stringers and αZr(O) columnar grains were not found for (U, Gd)O_2/Zr experiments. The zone I formed by (U, Gd)O_2/Zr experiments is more fragile than that by UO_2/Zr experiments. The boundary of zone I and zone II becomes indistinct with increasing reaction temperature.

The zone II appears to be a single phase of (U, Zr, Gd) solid solution with low gadolinium concentration. The appearance of this zone strongly depended on the reaction temperature. Though the uniform thickness of zone II was observed by the UO_2/Zr reaction, for (U, Gd)O_2/Zr reaction the thickness of zone II varied with the position, and the interface between zone I and zone II was indistinct and waving. At higher temperatures, large (U, Zr, Gd) globules were observed rather than uniform (U, Zr, Gd) layer.

The zone III for (U, Gd)O_2/Zr reaction was or αZr(O) containing no gadolinium and the morphology of this zone was the same as that for UO_2/Zr reaction. However, the proportion of zone III thickness to the whole reaction zones was obviously larger than that observed for UO_2/Zr reaction.

The thickness of each reaction zones was able to be

Table 1
Total layer thickness of UO_2/Zr and (U, Gd)O_2 reactions

Temperature (°C)	Reaction time (h)	Total layer thickness ($\times 10^{-6}$ m)					
		0 wt% G_d2O_3	1 wt% Gd_2O_3	2 wt% Gd_2O_3	4 wt% Gd_2O_3	6 wt% Gd_2O_3	8 wt% Gd_2O_3
1100	20	–	–	–	636	–	–
	30	–	–	–	929	–	–
	40	–	–	1090	986	910	–
	50	–	–	–	1090	–	–
1200	5	–	–	–	470	–	–
	10	936	–	–	820	–	–
	15	–	–	1130	884	1080	–
	20	–	–	–	1500	–	–
1300	2	743	–	–	781	–	–
	3	863	843	853	873	756	900
	5	1233	–	–	1170	–	–
	10	–	–	–	1710	–	–
1400	2	1010	–	920	920	1060	–
	3	1074	–	–	1010	–	–
	5	–	–	–	2210	–	–

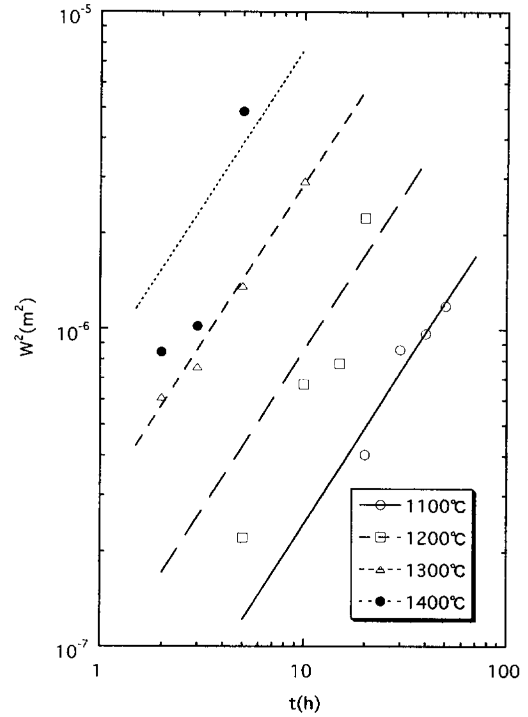

Fig. 2. Change in the layer thickness for (U, Gd)O_2 with the gadolina content of 4 wt%/Zr reaction with the reaction time.

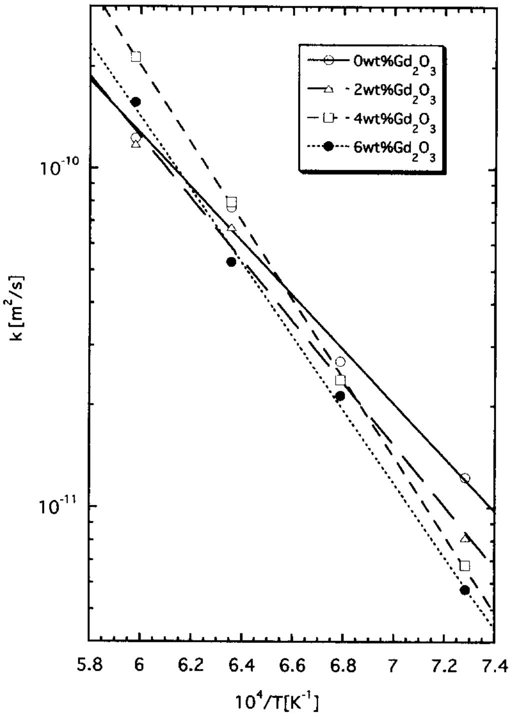

Fig. 3. Temperature dependence of the layer growth rate constant for UO_2 /Zr and (U, Gd)O_2 /Zr reactions.

measured for the UO_2/Zr reaction. The detailed data for the reaction zone growth kinetics for the UO_2/Zr reaction were published elsewhere [15]. Since the thicknesses of zone I and zone II formed for the (U, Gd)O_2/Zr reaction were not uniform, it was difficult to estimate the time dependence of each zone thickness. The total thicknesses of the reaction layer for the (U, Gd)O_2/Zr were evaluated and compared with the results for UO_2/Zr.

The total reaction layer thickness measured for (U, Gd)O_2/Zr were summarized in Table 1, together with a part of the results for UO_2/Zr. It is obvious from Table 1 that the thickness of the reaction layer depends on the reaction time, the reaction temperature and the gadolinia content. In Fig. 2, the relation of the layer thickness with the reaction time was shown for the reaction between (U, Gd)O_2 with the gadolinia content of 4 wt% and Zr. It is found from Fig. 2 that the reaction layer growth appears to obey the parabolic law: The relationship between the layer thickness and the reaction time can be expressed as

$$W^2 = kt,$$

where W is the layer thickness, t is the reaction time and k is the layer growth rate constant. The layer growth rate constants thus obtained are given in Table 2. The reaction temperature dependence of the layer growth rate constant

Table 2
Layer growth rate constants of UO_2/Zr and (U, Gd)O_2 reactions

Temperature (°C)	Growth rate constant, k (m^2/s)					
	0 wt% Gd_2O_3	1 wt% Gd_2O_3	2 wt% Gd_2O_3	4 wt% Gd_2O_3	6 wt% Gd_2O_3	8 wt% Gd_2O_3
1100	1.23×10^{-11}	–	8.19×10^{-12}	6.79×10^{-12}	5.75×10^{-12}	–
1200	2.70×10^{-11}	–	2.38×10^{-11}	2.38×10^{-11}	2.14×10^{-11}	–
1300	7.70×10^{-11}	6.58×10^{-11}	6.73×10^{-11}	7.98×10^{-11}	5.30×10^{-11}	7.50×10^{-11}
1400	1.23×10^{-11}	–	1.18×10^{-10}	2.14×10^{-10}	1.57×10^{-10}	–
k_0	9.79×10^{-6}	–	3.36×10^{-5}	1.69×10^{-3}	4.27×10^{-4}	–
E (kJ/mol)	156	–	173	221	207	–

$k = k_0 \exp(-E/RT)$, $R = 8.314$ (J/mol K).

Table 3
Temperature dependence of the layer growth rate constant of UO_2/Zr, UO_2/zircaloy and (U, Gd)O_2 reactions

Reaction	Temperature range (°C)	Growth rate equation $k = k_0 \exp(-E/RT)$	Author
UO_2/Zr	1000–1400	$k = 9.79 \times 10^{-6} \exp(-156000/RT)$	this work
(U, Gd)O_2/Zr 2wt%Gd_2O_3	1100–1400	$k = 3.36 \times 10^{-5} \exp(-173000/RT)$	this work
(U, Gd)O_2/Zr 4wt%Gd_2O_3	1000–1400	$k = 1.69 \times 10^{-3} \exp(-221000/RT)$	this work
(U, Gd)O_2/Zr 6wt%Gd_2O_3	1100–1400	$k = 4.27 \times 10^{-4} \exp(-207000/RT)$	this work
UO_2/Zr	704–1093	$k = 7.65 \times 10^{-6} \exp(-155000/RT)$	Mallett et al.
UO_2/zircaloy-4	1000–1700	$k = 1.62 \times 10^{-4} \exp(-189000/RT)$	Hofmann et al.
UO_2/zircaloy-2	677–1300	$k = 4.00 \times 10^{-4} \exp(-210000/RT)$	Rooney et al.
UO_2/zircaloy-2	1000–1500	$k = 2.66 \times 10^{-4} \exp(-199000/RT)$	Paul et al.

$R = 8.314$ J/mol K.

is shown in Fig. 3. As evidenced by Fig. 3, the temperature dependence of the growth rate constant is written as

$$k = k_0 \exp(-E/RT),$$

where E is the activation energy of the layer growth and R the gas constant. In Table 3, the estimated values of k_0 and E are listed for the UO_2/Zr and the (U, Gd)O_2/Zr reactions in the present study, together with the reported data for the reaction of UO_2 with zircaloy and Zr [1–6]. It is found from Fig. 3 and Table 2 that below a temperature of 1200°C, the growth rate constants were smaller for (U, Gd)O_2/Zr than for UO_2/Zr. As revealed in Table 3, the values for the activation energy for the layer growth for UO_2/Zr and UO_2/zircaloy are less than 20 kJ/mol and was smaller for (U, Gd)O_2/Zr obtained in the present study.

The theoretical analysis reported by Olander [11] suggests that the growth of zone I formed by UO_2/Zr is controlled mainly by diffusion of constituents in the columnar or αZr(O) zone and that compositions at the interfaces of UO_2/zone I and zone I/zone II also influence the growth of zone I. The zone I observed for the (U, Gd)O_2/Zr reaction was more complicated rather than that for UO_2/Zr reaction. For the (U, Gd)O_2/Zr reaction, the microstructure showed the presence of Zr(O) inclusions in the metallic (U, Zr, Gd) phases and the oxygen content of α Zr(O) at the UO_2/zone I and zone I/zone II interfaces may be quite different from those observed for the UO_2/Zr reaction. The difference in the layer growth rate between UO_2/Zr and (U, Gd)O_2/Zr reactions appears to be associated with the differences in the morphology and the composition of the existing phases in zone I.

Melting of the (U, Zr) phase formed by the reaction of UO_2 with Zr appears to occur at a temperature just above the melting point of pure uranium. Since the melting point of gadolinium is 1312°C, melting of the (U, Zr, Gd) phase coexisting with αZr(O) in zone I may occur at higher temperature rather than the (U, Zr) phase formed by the reaction of UO_2 with Zr. Whether the metallic phase is solid or liquid appears to cause the differences in the morphology and the composition of zone I between the (U, Gd)O_2/Zr and UO_2/Zr reactions. Further studies on equilibria in the U–Zr–Gd–O ternary system an diffusion analysis of (U, Gd)O_2/Zr reaction is required to clarify the influence of gadolinia addition into fuel on the high temperature reaction of doped-fuel with cladding.

4. Conclusions

The high temperature reaction of (U, Gd)O_2 with Zr was examined to obtain fundamental information about the influence of doped-gadolinia on the reaction kinetics and the morphology of UO_2 fuel with zircaloy cladding. The reaction between (U, Gd)O_2 with Gd_2O_3 contents from 1–8 wt% and Zr was performed in the temperature range between 1100 and 1400°C for 2–50 h in a vacuum below 10^{-5} Pa. For the UO_2/Zr reaction, typical three reaction zones, αZr(O) + (U, Zr), (U, Zr) and αZr(O), were observed, while for the (U, Gd)O_2/Zr reaction, the reaction layer also consisted of three zones, but the morphology of the reaction zones was slightly different from that of the UO_2/Zr reaction. The (U, Gd)O_2/Zr reaction obeyed the parabolic rate law, which is the same as that of UO_2/Zr reaction. The layer growth rate constants and the activation energies for the reaction were estimated from the experimental data. Below a temperature of 1200°C, the growth rate constants were smaller for (U, Gd)O_2/Zr than for UO_2/Zr. It was found that the activation energy for the layer growth was larger for (U, Gd)O_2/Zr than for UO_2/Zr. These differences appear to be closely related with liquid phase formation in zone I.

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