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Section 4. Basic properties

Thermodynamic analysis of chemical states of fission products in uranium–zirconium hydride fuel

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Abstract

The chemical state of fission products (FPs) in $U + ZrH_{1.60}$ fuel was studied from the thermodynamic point of view. Twenty most abundant FP elements were taken into account in the system of U–Zr–H–O–FP in which oxygen is treated as an impurity. The Thermo-Calc computer code was used to calculate the equilibrium state of the multi-phase and multi-component system. This calculation shows that yttrium, the alkaline earth metals (Ba, Sr) and most of the lanthanides prefer to form corresponding binary hydrides. Oxygen impurities in the system are likely to form a mixture of Y_2O_3, Pr_2O_3, Sm_2O_3 as well as Ce_2O_3 depending on their fission yields. With increasing of burn-up, only a slight decrease of the hydrogen potential in the fuel pin can be expected because of the very little consumption of hydrogen in the hydrogenation process of the FP. In the gas phase, H_2, Cs, Rb, CsRb as well as CsI are the main vapor species apart from the noble gases Xe and Kr. Solid swelling of the fuel due to formation of condensed phases was calculated as a function of burn-up.

1. Introduction

The irradiation behavior of fission products (FPs) has a strong influence on the physical properties of nuclear fuels. A fundamental investigation of the chemical state of a large variety of fission products in fuels is of great importance. Much research has been done on metal, oxide, nitride and carbide fuels for decades [1–4]. Similar investigations of uranium–zirconium hydride fuels are still limited although early irradiation effects were reported [5–8]. Recently, Wang and Olander [9] have made an extensive review and re-evaluation of the thermodynamics of the Zr–H system. A thermodynamic database related to zirconium alloys was established by Dupin et al. [10]. Their efforts made it possible to do further thermodynamic predictions of the chemical state of fission products in the $U + ZrH_{1.60}$ fuel. Their works are also helpful for the research and development of transmutation of long life minor actinide, such as Am and Np, by using hydrides in fast breeder reactors [11].

In the present paper, the chemical state of fission products in the $U + ZrH_{1.60}$ fuel was evaluated from the thermodynamic point of view. Twenty most abundant FP elements were taken into account in the system of U–Zr–H–O–FP. The Thermo-Calc computer code [12] was used to predict the thermodynamically favored phases in their equilibrium state. Solid swelling was estimated from the volume changes of condensed phases.

2. Calculation conditions

The Thermo-Calc computer code, developed by the Swedish Royal Institute of Technology, was utilized to make the thermodynamic calculation. This powerful software is suitable for chemical equilibrium calculations of multi-phase and multi-component systems. In the present study, 20 elements can be treated simulta-

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neously in one calculation. Therefore, the thermodynamic stability of each phase can be analyzed in more detail than by early common methods in which one typical species is often chosen to represent other similar ones.

The elemental inventory of each fission product in $U + ZrH_{1.60}$ fuel is estimated by the Origen 2.1 computer code for operating conditions of PWR [13]. The amount of oxygen as an impurity in zirconium hydride is assumed to be 1000 ppm. It most probably exists mainly in form of ZrO_2 on the surface of zirconium hydride. Dissolved oxygen in uranium is neglected because the amount is relatively small. The calculations are made in the temperature range from 673 to 1273 K, a typical operating condition of hydride fuel. Fuel compatibility with the cladding materials is not discussed here. Further information about the fuel was described in a previous paper of the authors [14].

The thermodynamic data of all the possible species and phases in the U–Zr–H–O–FP system were loaded preferentially from the assessed databases of Scientific Group Thermodata Europe (SGTE) [15]. For missing Gibbs energy data of phases of interest, the authors made their own estimation or reproduced data as shown in Table 1. In total, over 170 species and 130 phases were included in the calculations, such as binary hydrides, complex oxides and other compounds of uranium, zirconium, cesium, rubidium, iodine and tellurium. Ternary hydrides were not considered here because very little data can be found in publications.

3. Calculation results

3.1. Vaporization properties of volatile fission products

When thermodynamic equilibrium states are established in the system, the main vapor species are found to be Xe(g), Kr(g), Cs(g), Rb(g), CsRb(g), H_2(g) as well as CsI(g) as shown in Fig. 1. Temperature has a great influence on partial vapor pressures of the volatile fission products. For high temperatures over 1000°C, a large amount of hydrogen may release from the hydrides and consequently cause a considerable increase of total inner pressure. This indicates that hydrogen partial pressure is one of the most critical factors, and operating temperature must be strictly controlled. Another interesting point is that the partial vapor pressures of barium- and strontium-bearing vapor species are a few orders of magnitude lower than those of the alkaline metals Cs(g) and Rb(g). The reason is that Ba and Sr react with hydrogen to form stable hydrides as discussed later in Section 4.1. The calculation also shows that oxygen pressure is extremely low. It is about 3×10^{-55} Pa at 10 000 MWd/t and about 1×10^{-55} Pa at 50 000 MWd/t, respectively.

3.2. Condensed phases of fission products

The calculations show that stable condensed phases in $U + ZrH_x$ fuel can be classified in the following four ways:

Table 1
Gibbs energy parameters of selected phases and species

Phase	Gibbs energy (J/mol), $G(T) = a + bT + cT \ln T + dT^2 + e/T + fT^3$					
	a	*b*	*c*	*d*	*e*	*f*
YH_3	−266 427	222.14	−38.74	-7.74×10^{-3}	0	0
YH_2	−233 926	190	32.8	-10.625×10^{-3}	2.09×10^{5}	0
LaH_2	−213 676	215.7	−39.25	-7.575×10^{-3}	0	0
SmH_2	−212 028	202.8	−38.0	-7.85×10^{-3}	0	0
PdH	−184 000	−58.6	0	0	0	0
UI_4	−569 278	736.8	−145.6	-4.979×10^{-3}	987 425	0
UI_3	−499 790	488.8	−105.02	-1.21×10^{-2}	0	0
URu_3	−185 763	541.4	−101.2	-9.24×10^{-3}	233 619	0
URh_3	−288 436	462.3	−88.51	−0.0304	0	2.74×10^{-6}
UPd_3	−553 996	600	−98.96	-5.5175×10^{-3}	12.83	-2.558×10^{-8}
$ZrTe_2$	−316 663	363.5	−72.14	-6.21×10^{-3}	75 224	0
Zr_2U	−33 384	520.6	−98.3	3.97×10^{-2}	385 950	-1.90×10^{-5}
Zr_2Pd	−126 000	−115.6	0	0	0	0
$ZrPd_2$	−233 400	−142	0	0	0	0
$ZrPd_3$	−346 400	−208	0	0	0	0
UTe	−198 056	247.2	−52.9	-3.2×10^{-3}	0	0
U_3Te_4	−648 000	−360	0	0	0	0
UTe_2	−318 000	−150	0	0	0	0
$RuTe_2$	−168 757	485.34	−86.48	1.14×10^{-2}	317 775	-2.91×10^{-6}
SmTe	−405 845	248.24	−51.53	-1.22×10^{-3}	7530	-4.213×10^{-7}

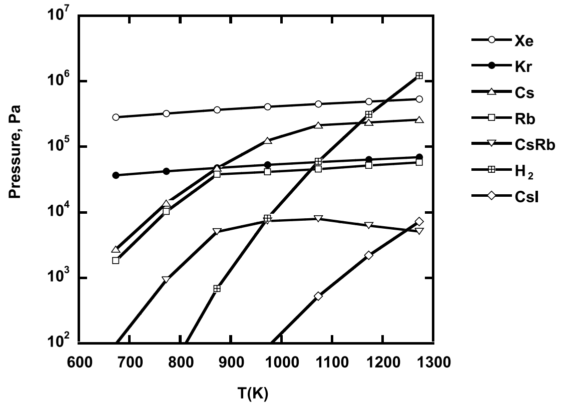

Fig. 1. Partial vapor pressures of the main vapor species calculated for U–Zr–H–O–FP system at 10 000 MWd/t U at 873 K.

(1) *Binary hydrides*. Zirconium and alkaline earth metals (Ba, Sr) prefer to form stable binary hydrides. The lanthanides fission products are most likely to exist in the corresponding binary hydrides, i.e., LaH_2, NdH_2 (see Fig. 2). They occupy about 40% volume of the whole solid FP compounds.

(2) *Oxides*. Possible oxides are Y_2O_3, Sm_2O_3, Pr_2O_3 and Ce_2O_3 in decreasing order of priority of formation. The concentrations of these oxides are varying as a function of burn-up because of different yield rates of the fission products. Oxidation of Sm, Pr and Ce, is possible only when the amount of Y is not enough to combine all the oxygen at low burn-ups. One typical example at 873 K is shown in Fig. 3.

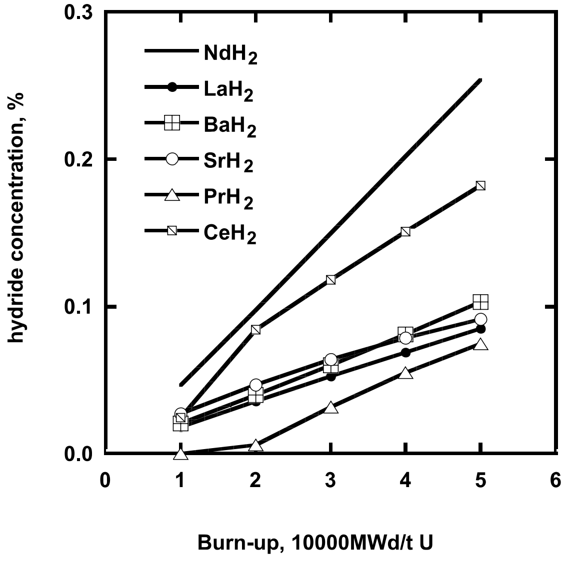

Fig. 2. Hydride concentration as a function of burn-up at 873 K.

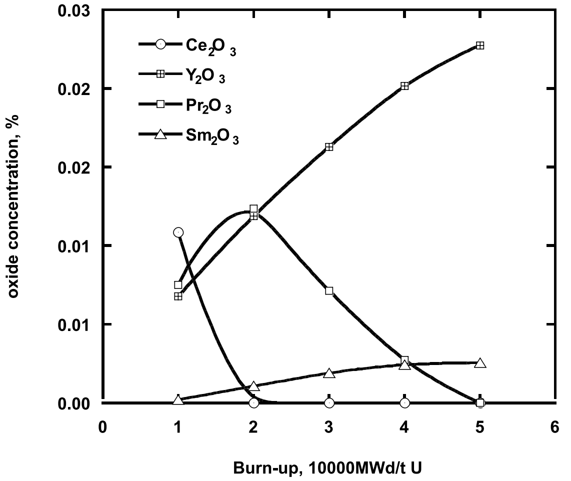

Fig. 3. Oxide concentration as a function of burn-up at 873 K.

(3) *Noble metals and uranium*. The possible phases are elemental Mo, Tc and U, stable compounds of URh_3(s), URu_3(s), UPd_3(s) and UPd_4 solid solutions among them. Noble metals act similar to the way they do in oxide fuels.

(4) *Compounds including cesium, rubidium, iodine and tellurium*. In this category, Cs(l), Rb(l), CsI(s) and SmTe(s) can be found in the hydride fuel. Cesium has multiple chemical forms because of its relatively large yield compared with other fission products.

3.3. Swelling due to formation of low density compounds

Solid swelling results from the formation of low density compounds in the fuel. The volume change $\Delta V/V_0$ of the fuel was obtained by computing the change of each phase corresponding to the irradiation extent

$$\frac{\Delta V}{V} = \frac{\left(V_{U} - V_{U'}\right) + \left(V_{ZrH} - V_{ZrH'}\right) + \sum_i V_{FP_i} - V_{ZrO_2}}{V_{U} + V_{ZrH} + V_{ZrO_2}}, \tag{1}$$

where V_U and V_{ZrH} are the initial volume of uranium and zirconium hydride, respectively. $V_{U'}$ and $V_{ZrH'}$ are their corresponding volumes after irradiation. V_{FP_i} is the volume of the *i*th condensed phase of fission products after irradiation. V_{ZrO_2} is the initial volume of zirconium oxide. The X-ray densities of the phases from the JCPDS files were utilized to calculate the volume change of each phase.

According to the results of the present thermodynamic calculations, the solid swelling of the $U + ZrH_x$ fuel as a function of burn-up is shown in Fig. 4. For example, it is about 0.45% at 10 000 MWd/t U for 45 wt% $U + ZrH_x$. This value is even close to those of UO_2, (U,Pu)N and (U,Pu)C [2–4]. Simnad et al., however,

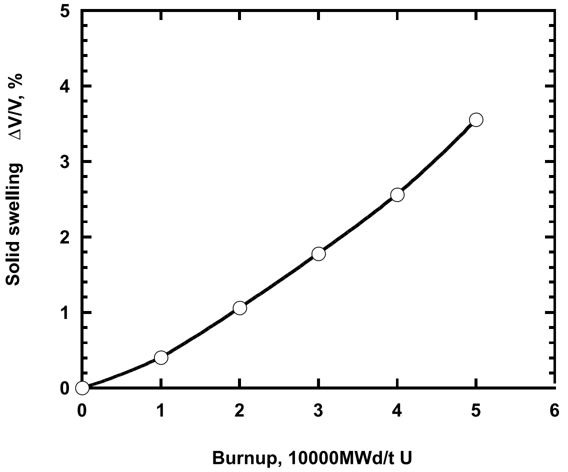

Fig. 4. Calculated solid swelling of 45 wt% $U + ZrH_{1.6}$ as a function of burn-up at 873 K.

reported a high solid swelling rate of 1.2–2.3% per 1% burn-up of U for 10 wt% $U + ZrH_{1.6}$ [7,8]. It seems that they overestimated the solid swelling compared to the present results. Furthermore, the solid swelling rate of hydride fuel is much lower than its total swelling value of about 3–5% [7,8]. This indicates that formation of void and radiation-induced fuel growth may be the main contributor to volume increase instead of formation of solid fission products.

4. Discussion

4.1. Comparison of thermodynamic stability of selected hydrides

To analyze the stability of hydrides, a comparison of hydrogen dissociation pressures was made as listed in Table 2. It can be seen that P_{UH_3}, P_{CsH} and P_{RbH} are much higher than that of matrix $ZrH_{1.6}$ by a few orders of magnitude. In contrast, those of rare earth hydrides are much lower than that of $ZrH_{1.6}$. The priority of hydride formation should be as the following:

$$\begin{aligned} YH_2(s) &> LaH_2(s) > NdH_2(s) > SmH_2(s) > BaH_2(s) \\ &> PrH_2(s) > CeH_2(s) > SrH_2(s) > ZrH_{1.60}(s). \end{aligned}$$

That is why U, Cs and Rb cannot form stable hydrides in this condition while the other rare earth metals prefer to form hydrides. It also helps us to understand that Ba and Sr are not so volatile as Cs and Rb at this ambient condition because the corresponding hydrides of alkaline earth metals are very stable.

Table 2
Comparison of hydrogen dissociation pressures over metal hydrides at 800 K

Hydrides	Pressure (Pa)
RbH	5.86×10^6
CsH	2.74×10^6
UH_3	1.26×10^6
$ZrH_{1.6}$	1.17×10^2
SrH_2	2.70
CeH_2	1.55
PrH_2	8.66×10^{-1}
SmH_2	6.33×10^{-1}
BaH_2	4.76×10^{-1}
NdH_2	3.29×10^{-1}
LaH_2	1.49×10^{-1}
YH_2	9.58×10^{-1}

4.2. Effect of burn-up on hydrogen potential in the hydride fuel

Hydrogen pressure is one of the most important parameters that limit the operation of the hydride fuel. In Fig. 5, the partial vapor pressure of hydrogen and hydrogen content in δ-ZrH_x were plotted as a function of burn-up. It is clear that the hydrogen potential in the system decreased with increasing burn-up. The average hydrogen content in zirconium hydride is also reduced to $ZrH_{1.6-x}$ with the accumulation of fission products. This is because hydrides of some fission products like rare earths are thermodynamically more stable compared with zirconium hydride, as discussed above. So, zirconium hydride has to release a small amount of hydrogen to FP hydrides. Since the amount of FP is much less than that of ZrH_x, this results in only a slight decrease of hydrogen potential for the whole system. For example, an initially uniform $ZrH_{1.60}$ may change to $ZrH_{1.55}$ at a burn-up of 50 000 MWd/t U at 873 K.

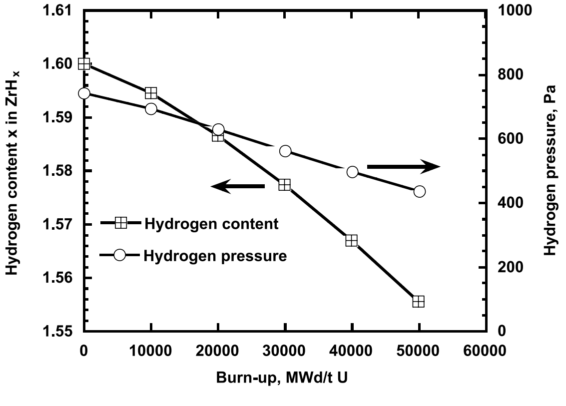

Fig. 5. Hydrogen content in the δ-ZrH_x and partial vapor pressure of hydrogen as a function of burn-up at 873 K.

5. Conclusions

The chemical states of fission products in $U + ZrH_x$ fuel were studied from the thermodynamic point of view. The 20 most abundant elements were taken into account in the system of U–Zr–H–O–FP. The Thermo-Calc computer code was used to make the multi-phase multi-component calculations.

1. The calculations showed that yttrium, alkaline earth metals (Ba, Sr) and most of lanthanide series prefer to form corresponding binary hydrides. Oxides that can exist in the system are likely to be a mixture of Y_2O_3, Pr_2O_3, Sm_2O_3 as well as Ce_2O_3 depending on their affinity to oxygen.
2. Uranium and noble metals (Mo, Tc, Ru, Rh and Pd) prefer to remain in their elemental state except for the formation of URu_3(s), URh_3(s) and UPd_3(s). The other stable solid phases would be CsI(s) and SmTe(s). In gas phase, H_2, Cs, Rb, CsRb as well as CsI are the main vapor species apart from inert gases. With increasing of burn-up, only a slight decrease of hydrogen potential in the core can be expected because of the very little consumption of hydrogen in the hydrogenation of FP.
3. Solid swelling due to the formation of solid fission products was predicted as a function of burn-up. For 45 wt% $U + ZrH_{1.6}$, it is estimated to be about 0.45% at 10 000 MWd/t U.

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The authors would like to express special thanks to Professor C. Lemaignan (CEA–Grenoble DEC, France), Professor I. Ansara (LTPCM ENSEEG, Dominaine Universitaire, France) and their colleagues for providing the Thermo-Calc compatible Zr–H database. Mr Y. Nakajima of the Japan Nuclear Cycle Development Institute gave great help to calculate fission products yield by the ORIGEN computer code.

Appendix A. Thermodynamic data of selected compounds

Zr–H: This binary system was well developed by Dupin et al. [10]. Their database was employed as a fundament of the present calculation.

U–Te: Values of the standard enthalpy and entropy of UTe(s) were taken from [16], i.e., $\Delta_f H^\circ = -182$ kJ/mol, $S(298.15) = 109$ J/K mol. The heat capacity was estimated as $C_p(T) \approx 52.9 + 6.4 \times 10^{-3} \times T$ by the authors from the data of USe(s) [17] assuming a similar temperature effect.

U–I: Values of the parameters in Gibbs energy $G(T)$ of UI_4 and UI_3 were taken from the data of standard enthalpy, entropy and heat capacity reported by Wanner and Forest [18].

(Ru, Sm)–Te: Values of the parameters in Gibbs energy $G(T)$ of $RuTe_2$ and SmTe were from the data of standard enthalpy, entropy and heat capacity reported by Chattopadhyay and Juneja [19].

UZr_2: Heat capacity of UZr_2 was taken from [20]. The standard enthalpy of formation of about −4 kJ/mol reported in [21] was employed. The authors estimated S (298.15) to be about 42.7 J/K mol from the entropy values of corresponding elements.

(Y, La)–H: Values of the parameters in Gibbs energy $G(T)$ of YH_2, YH_3 and LaH_2 were computed based on the data of standard enthalpy, entropy and heat capacity in [22].

Zr–Te: Values of the parameters in Gibbs energy $G(T)$ of $ZrTe_2$ were from the data given by Cordfunke and Konings [23].

Zr–Pd: Values of the parameters in Gibbs energy $G(T)$ of Zr_2Pd, $ZrPd_2$ and $ZrPd_3$ were roughly estimated by the authors based on the limited data given in [24].

SmH_2(s): The standard enthalpy of SmH_2(s) was recomputed as about −200 kJ/mol from [25]. The entropy S (298.15) and heat capacity were estimated by the authors from the values of LaH_2(s), CeH_2(s), PrH_2(s) and NdH_2(s). $S\,(298.15) \approx 56.4$ J/K mol. $C_p(T) \approx 37.9 + 16 \times 10^{-3} T$.

$U{-}(Ru, Rh, Pd)_3$: Latest data of URu_3 in [26] and UPd_3 in [27] were used to calculate their Gibbs energy $G(T)$ while that of URh_3 was taken from [23] given by Cordfunke and Konings. UPd4 is not considered because its Gibbs energy of formation is very close to that of UPd3 given by the same authors [28].

Pd–H: The data of PdH were roughly estimated by the authors due to the fact that it decomposes around 410 K.

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