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A study on the Thermodynamic Reactions between Carbon layer and UO_2 Kernel in VHTR Fuels

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1. Introduction

VHTR will be one of important reactors in the near future because it can produce hydrogen as well as electric power efficiently. VHTR fuel is operated under high temperature, and the reaction between carbon layer and uranium dioxide kernel can be a problem. CO and CO_2 generated by chemical reactions cause the increase of internal pressure, and carbon layer can be damaged. In this study, we studied the thermodynamic equilibrium between uranium dioxide kernel and carbon layer at high temperature and discussed about the safety of VHTR fuel.

2. Method and Results

In this section, we describe equations of reactions in different temperature ranges. Also, calculation tools (Solgasmix-PV, HSC) are described as well as reaction models.

2.1 Equation of Reaction

Uranium, oxygen and carbon react differently depending on the changing of temperature. If the temperature is over 2000℃, uranium and oxygen, carbon reacts according to the following equations.

$$C + \frac{1}{2}O_2 = CO \quad (1)$$

$$CO + \frac{1}{2}O_2 = CO_2 \quad (2)$$

$$UO_2 = UO_{2-x} + \frac{x}{2}O_2 \quad (3)$$

In this study, UO_{2-x} is assumed as a mixture of UO_2 and UO. On the other hand, the model of uranium dioxide can dissociate into metal(U) if temperature is less than 2000℃.

$$UO_2 = U + O_2 \quad (4)$$

2.2 Solgasmix-PV

The Solgasmix-PV is a computer code to calculate the equilibrium state by finding the minimum of total Gibbs free energy.

According to the definition of Gibbs free energy, a variation amount of Gibbs free energy gives the following expression:

$$dG = -SdT + VdP \quad (5)$$

At a constant temperature, the expression of dG for ideal gas is

$$dG = \frac{RT}{P}dP \quad (6)$$

$$G = RT \ln P \quad (7)$$

In general, the Gibbs free energy of species i gives following expression.

$$G_i = G_i^o + RT \ln a_i \quad (8)$$

Total Gibbs free energy of a system can be expressed:

$$G_T = \sum_i n_i (G_i^o + RT \ln a_i) \quad (9)$$

First, this program performs computation of mass conservation of each element. If the mass conservation works well, the Solgasmix-PV carries out calculation and shows the equilibrium states that is the minimum of total the Gibbs free energy of the system.

2.3 Calculation and Results

$UO_{2\pm x}$ exist in a huge region of non-stoichiometric range. If $UO_{2\pm x}$ follow Equation (3), variation of the Gibbs free energy for $UO_{2\pm x}$ gives the following expression.

$$\overline{\Delta G_{O_2}}(T, x) = RT \ln P_{O_2} \quad (10)$$

This equation is a function of temperature and non-stoichiometry, y. Because of the additional variable (x), we cannot directly apply Eq (10) to Solgasmix-PV or HSC. To resolve this difficulty, we assumed that UO_{2-x} is a mixture of UO_2, UO, and U. To conform the mixture model, we compared the experimental oxygen potential and that from the mixture model at the temperature, 1000℃~2100℃. Calculated oxygen potentials were reasonably well matched to the experimental values in the range, O/U=1.9~2.1. Based on these results, we assume UO_{2-x} as a mixture of UO_2 and UO.

We assume the carbon layer and the UO_2 kernel are chemically equilibriated at a given temperature. For the comparison purposes, we changed the ratio of the amounts of carbon to that of UO_2 from 10^{-2} to 1.

Figure 1~3 show the calculation results. Above 1800℃ UO_2 becomes partially unstable. Therefore, part of UO_2 is divided into uranium and oxygen. Then, oxygen becomes CO_2 or CO by reacting with carbon. Also, uranium metal becomes UC by reacting with carbon. Because of this reason, amount of carbon falls sharply and amount of CO_2 or CO increase rapidly above 1800℃.

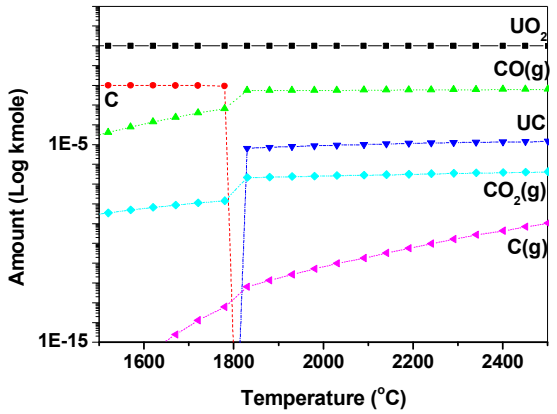

Figure 1. Variation of C, C(g), CO(g), CO_2(g), UC, UO_2 in system for C:UO2=0.01:1.

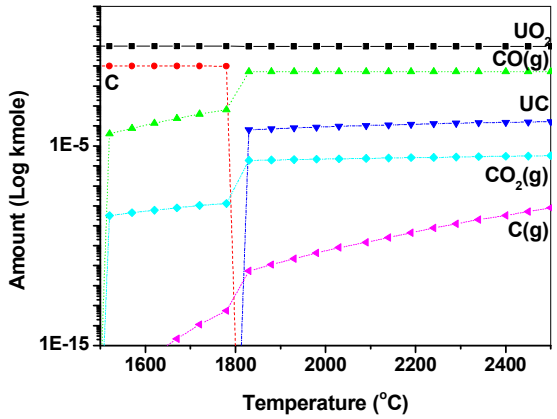

Figure 2. Variation of C, C(g), CO(g), CO_2(g), UC, UO_2 in system for C:UO2=0.1:1.

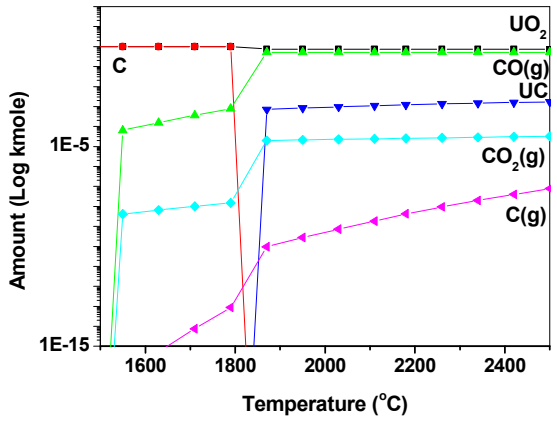

Figure 3. Variation of C, C(g), CO(g), CO_2(g), UC, UO_2 in system for C:UO2=1:1.

According to the calculation results, carbides are thermodynamically active above 1800℃. Hence, the fuel containing UO_2 kernel and carbon layer should be used under the temperature of 1800℃.

3. Conclusion

Thermodynamic stability of VHTR fuel containing UO_2 kernel and carbon layer was studied using Solagasmix-PV and HSC program. Above 1800℃, carbon compounds start to form in the fuel, which might be the reason for fuel instability at accident conditions. More thermodynamic and kinetic studies seems to be needed for further analyses under accident conditions.

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