Thermodynamic Equilibrium Calculation of ZrC in the Zr-salts/CH$_4$/H$_2$ Systems for the Fabrication of ZrC TRISO Coated Particles

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1. Introduction

To develop the competitive power of HTGR, increases in the power density and efficiency are inevitable. The higher performance of fission product retention of the coated fuel particles at high temperatures is required. Although SiC has excellent properties, it gradually loses mechanical integrity at very high temperatures, especially above 1700°C, by thermal dissociation [1]. The SiC coating layer is also attacked chemically by fission product palladium whose yield from ^{239}Pu is about tenfold that from ^{235}U [2].

Zirconium carbide (ZrC) is known as a refractory and chemically stable compound, having a melting point of 3540°C, and melts eutectically with carbon at 2850°C. In addition, it has a higher resistance to the chemical attack by fission product elements such as palladium and appears to be a better barrier to cesium in post-irradiation heating experiments [2]. The ZrC coating layer is a candidate to replace the SiC coating layer of the TRISO-coated fuel particle [1].

For the fabrication of the ZrC TRISO coated particles by the fluidized CVD process, some Zr-salts, such as zirconium chloride (ZrCl$_4$) [3,4], zirconium bromide (ZrBr$_4$) [5], zirconium iodide (ZrI$_4$) [6], etc., were used as source materials with hydrocarbon.

One of the evaluation methods for the feasibility of a particular coating system is a thermodynamic calculation of equilibrium of the chemical species with process parameters, such as the input gas ratio, reaction temperature, total pressure, etc. The SOLGASMIX-PV is a widely used computer program for calculating the equilibrium in a chemical system [7].

In this paper, we calculated the equilibrium mole fraction of ZrC with the input gas ratios and deposition temperatures in the different Zr-salts/CH$_4$/H$_2$ systems by the SOLGASMIX-PV program. The Zr-salts included ZrCl$_4$, ZrBr$_4$ and ZrI$_4$. Based on the calculated results, we suggested the initial process conditions of the each system to deposit the ZrC layer for the fabrication of the ZrC TRISO particles.

2. Themodynamic Calculation by SOLGASMIX-PV

The equilibrium relationships in the complex chemical systems were calculated by the SOLGASMIX-PV program. Chemical equilibrium calculations involve finding the system composition, within certain constraints, which contains the minimum free energy. The constraints are the preservation of the masses of each element present and either the constant pressure or

volume. Any species that can be formed from the reactants is considered based on available data[7]. All fundamental thermochemical data were extracted from the JANAF tables [8].

The SOLGASMIX-PV can calculate equilibria in the systems containing a gaseous phase, condensed phase solutions, and condensed phases of invariant and variable stoichiometry [7]. For our considering systems of Zr-salts-CH$_4$, the database contains the Gibbs energy coefficients for the 40~44 gaseous compounds and for the 9 condensed stoichiometric phases as described in the Table 1, respectively.

Table 1. Chemical species considered in the thermo-dynamic equilibrium calculations.

System		Chemical Species
ZrCl$_4$-CH$_4$	Condensed Phase (9 species)	C(GR), C$_7$H$_8$(L), C$_8$H$_{18}$(L), Zr(A), Zr(B), Zr(L), ZrC(S), ZrC(L), ZrCl$_2$(L)
	Gaseous Phase(44 species)	C, CCl, CCl$_2$, CCl$_3$, CCl$_4$, CH, CH$_2$, CH$_3$, CH$_4$, CH$_3$Cl, C$_2$, C$_2$Cl$_2$, C$_2$H , C$_2$H$_2$, C$_2$H$_3$, C$_2$H$_4$, C$_2$H$_5$, C$_2$H$_6$, C$_3$, N-C$_3$H$_7$, I-C$_3$H$_7$, C$_3$H$_8$, C$_4$, N-C$_4$H$_{10}$, I-C$_4$H$_{10}$, C$_5$, C$_6$H$_5$, C$_6$H$_6$, C$_7$H$_8$, C$_8$H$_{16}$, N-C$_8$H$_{18}$, O-C$_{12}$H$_9$, C$_{12}$H$_{10}$, Cl, Cl$_2$, H, HCl, H$_2$, Zr, ZrCl$_4$, ZrCl, ZrCl$_2$, ZrCl$_3$
ZrBr$_4$-CH$_4$	Condensed Phase (9 species)	Br$_2$(L), C(GR), C$_7$H$_8$(L), C$_8$H$_{18}$(L), Zr(A), Zr(B), Zr(L), ZrC(S), ZrC(L)
	Gaseous Phase (41 species)	Br, Br$_2$, C, CH, CH$_2$, CH$_3$, CH$_4$, C$_2$, C$_2$H, C$_2$H$_2$, C$_2$H$_3$, C$_2$H$_4$, C$_2$H$_5$, C$_2$H$_6$, C$_3$, N-C$_3$H$_7$, I-C$_3$H$_7$, C$_3$H$_8$, C$_4$, N-C$_4$H$_{10}$, I-C$_4$H$_{10}$, C$_5$, C$_6$H$_5$, C$_6$H$_6$, C$_7$H$_8$, C$_8$H$_{16}$, N-C$_8$H$_{18}$, I-C$_8$H$_{18}$, O-C$_{12}$H$_9$, C$_{12}$H$_{10}$, H, HBr, H$_2$, Zr, ZrBr, ZrBr$_2$, ZrBr$_3$, ZrBr$_4$, CBr, CBr$_4$, HZr
ZrI$_4$-CH$_4$	Condensed Phase (9 species)	C(GR), C$_7$H$_8$(L), C$_8$H$_{18}$(L), I$_2$(L), Zr(A), Zr(B), Zr(L), ZrC(S), ZrC(L)
	Gaseous Phase(40 species)	C, CH, CH$_2$, CH$_3$, CH$_4$, C$_2$, C$_2$H, C$_2$H$_2$, C$_2$H$_3$, C$_2$H$_4$, C$_2$H$_5$, C$_2$H$_6$, C$_3$, N-C$_3$H$_7$, I-C$_3$H$_7$, C$_3$H$_8$, C$_4$, N-C$_4$H$_{10}$, I-C$_4$H$_{10}$, C$_5$, C$_6$H$_5$, C$_6$H$_6$, C$_7$H$_8$, C$_8$H$_{16}$, N-C$_8$H$_{18}$, I-C$_8$H$_{18}$, O-C$_{12}$H$_9$, C$_{12}$H$_{10}$, H, HI, H$_2$, I, I$_2$, Zr, HZr, ZrI, ZrI$_2$, I$_2$, ZrI$_3$, ZrI$_4$

3. Results and Discussion

To make the ZrC TRISO coated particles, the fluidized CVD process is applied. For ZrC deposition, the input gas ratio (α) of H2/Zr-source gas (ZrCl$_4$ or ZrBr$_4$ or ZrI$_4$), another input gas ratio (β) of Zr/(CH$_4$+Zr-source), the total pressure, the deposition temperature should be considered as the process parameters. In the fluidized CVD system, the total pressure is fixed at 1 atm to make a fluidization bed

with a normal spout of spheres. We calculated the equilibrium mole fractions of ZrC with the input gas ratios and the deposition temperatures at 1 atm.

Fig. 1 shows the calculated results of the CH_4-H_2-$ZrCl_4$ (a), $ZrBr_4$ (b), ZrI_4 (c) with β's at P=1atm and α=100.
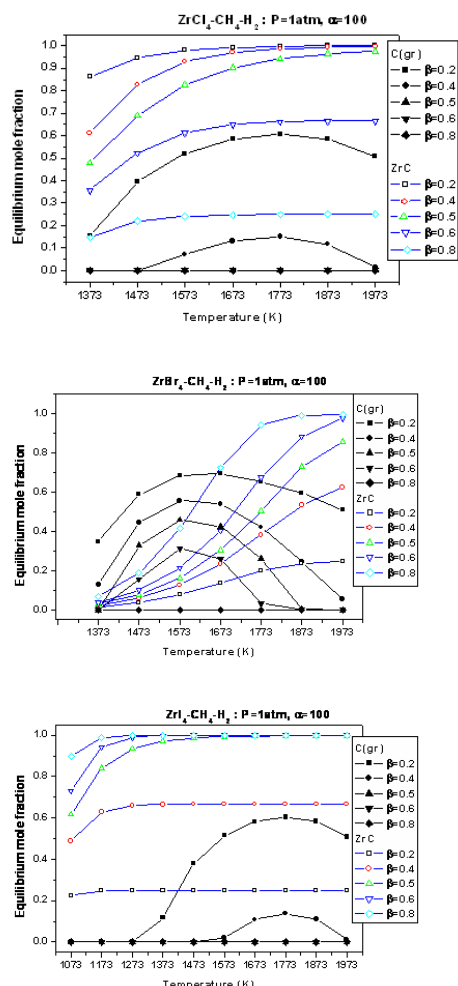

Fig. 1. The equilibrium mole fraction of ZrC with different β at P = 1 atm and α=100 in the different Zr-sources systems with CH_4-H_2 : (a) $ZrCl_4$, (b) $ZrBr_4$ and (c) ZrI_4.

In the $ZrCl_4$ system, the deposition temperature should be increased more than 1500°C at the βof less than 0.4 to obtain ZrC without excess C. On the other hand, a higher temperature of more than 1700°C is needed at the β of more than 0.6 in the $ZrBr_4$ system and a lower temperature of more than 1200°C is enough to obtain ZrC at the β of more than 0.6 in the ZrI_4 system.

Fig. 2 shows the calculated results of the CH_4-H_2-$ZrCl_4$ (a), $ZrBr_4$ (b), ZrI_4 (c) with different α at P=1atm and β=0.5. To obtain ZrC without excess C, the α of more than 500 is needed at the higher temperatures of 1600°C and 1700°C in the $ZrCl_4$ and $ZrBr_4$ system, respectively. On the other hand, ZrC could be obtained more than 1200°C irrespective of α in the ZrI_4 system.
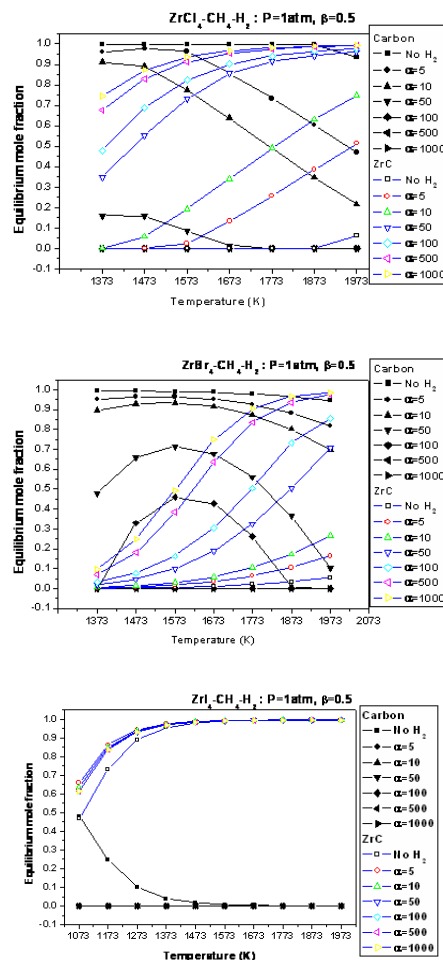

Fig. 2. The equilibrium mole fraction of ZrC with different α at P = 1 atm and β =0.5 in the different Zr-sources systems with CH_4-H_2 : (a) $ZrCl_4$, (b) $ZrBr_4$ and (c) ZrI_4.

4. Summary

Using the SOLGASMIX-PV program, we can easily evaluate the equilibrium mole fraction of ZrC in the CH_4-H_2-Zr-salts for the deposition of the ZrC layer. Based on the calculation results, we will suggest the appropriate process parameters for the fabrication of the ZrC TRISO particles.

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