Study on Chemical Vapor Deposition of Ultra High Temperature Ceramics Based on Prediction of Thermodynamic Equilibrium Phases

Daejong Kim*, Jangwon Han, Hyun-Geun Lee, Ji Yeon Park, Weon-Ju Kim
Korea Atomic Energy Research Institute, Nuclear Materials Development Div., 989-111Daedeok-daero, Yuseong-gu, Daejeon 305-353
**Corresponding author: dkim@kaeri.re.kr*

1. Introduction

Ultra high temperature ceramics (UHTCs) such as ZrB_2, HfB_2, ZrC, HfC, and TaC have extremely high melting points above 3000K [1,2]. They have excellent resistance to chemical attack, corrosion, and mechanical/thermal stress. Also, some UHTCs show good neutron characteristics. For example, ZrC has low neutron absorption cross section while HfB_2 has high neutron absorption cross section. Therefore, they can be used as constituent coating layer of TRISO fuel particles and neutron shielding materials [3]. In this study, we calculated thermodynamic equilibrium phases in $HfCl_4$-C_3H_6-H_2 system and derived optimal deposition conditions. Based on the calculation we tried to deposit a single HfC phase at a low temperature of 1200°C.

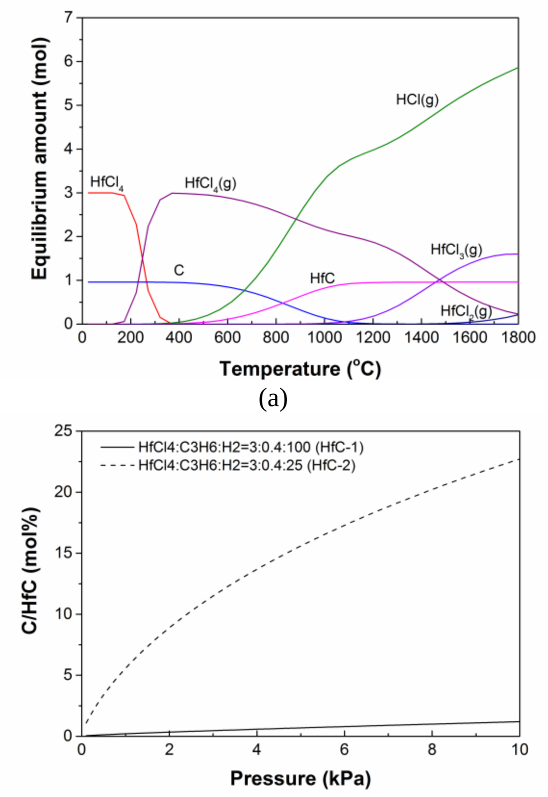
2. Methods and Results

2.1 Thermal Equilibrium Calculation

We used the HSC Chemistry 9.0 software to calculate thermodynamic equilibrium phases in the $HfCl_4$-C_3H_6-H_2 system. Following equations shows the reactions in the $HfCl_4$-C_3H_6-H_2 system.

$$HfCl_4(g) + H_2(g) + 1/3C_3H_6(g) = HfC(s) + 4HCl(g);$$
$$1/3C_3H_6(g) \rightarrow C(s) + H_2(g)$$
$$HfCl_4(g) + 2H_2(g) \rightarrow Hf(s) + 4HCl(g)$$
$$C(s) + Hf(s) \rightarrow HfC(s)$$

Fig. 1 shows the equilibrium phases depending on the temperature at 1200°C, 6.7 kPa. HfC begins to form at about 500°C and $HfCl_4$:C_3H_6:H_2 = 3:0.32:100. A near-single phase HfC forms above 1200°C, as shown in Fig. 1(a). Fig. 1(b) shows the C/HfC ratio in HfC-1 and HfC-2 deposition conditions. The amount of excess carbon decreases as H_2 increases.



(a)
(b)

Fig. 1. (a) Equilibrium phases and (b) C/HfC ratio in the $HfCl_4$-C_3H_6-H_2 system [4].

2.2 Chemical Vapor Deposition of HfC

Deposition was performed at 1200°C and 6.7 kPa based on thermodynamic equilibrium calculation results. Table I shows the chemical vapor deposition conditions.

Table I: Deposition Conditions of HfC

Sample designation	Flow rate (sccm)			
	C_3H_6	H_2	Ar	$HfCl_4$
HfC-1	10	3200	0	91
HfC-2	10	800	0	91

Fig. 2 shows the XRD results of HfC deposited at 1200°C. At the high ratio of H_2/($HfCl_4$+C_3H_6), a nearly single HfC phase was deposited, but a small amount of excess carbon was co-deposited in HfC at the lower ratio of H_2/($HfCl_4$+C_3H_6).

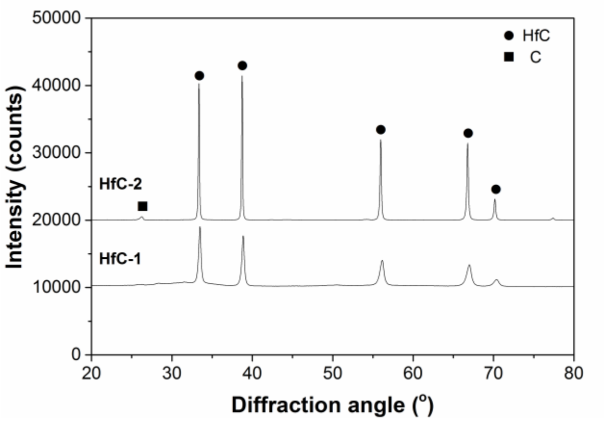
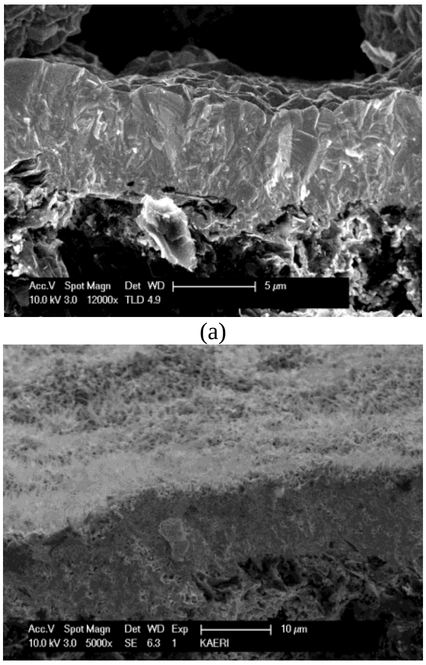


Fig. 2. X-ray diffraction peaks of hafnium carbides.

Fig. 3 shows the cross-sectional microstructure of the HfC coating layers of HfC-1 and HfC-2. HfC deposited in the HfC-1 condition contains many pores and the grain size is small. Also, HfC nanorods with a diameter of several hundred nanometers were grown. On the other hand, in the HfC-2 condition, HfC has a dense structure without pores, and the grain is coarse.



(a)

(b)

Fig. 3. Microstructures of HfC coatings: (a) HfC-1 and (b) HfC-2.

3. Conclusions

HfC was deposited at 1200°C by chemical vapor deposition from $HfCl_4$-C_3H_6-H_2 which was derived from thermodynamic calculation. a single HfC phase without excess carbon, was deposited at a high ratio of $H_2/(HfCl_4+C_3H_6)$. However, a porous HfC coating layer was formed. On the other hand, dense HfC was deposited at the low ratio of $H_2/(HfCl_4+C_3H_6)$ although it contains a small amount of excess in the HfC coating.

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