Improvement of Homogeneity of the ZrC Film by Controlling the Vaporizer temperature

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1. Introduction

One of the promising directions in the hydrogen production is advanced nuclear technologies based on the very high-temperature gas-cooled reactors (VHTR). This reactor types should provide core-output He gas temperature on a level of 1000°C. One of solutions to realize this requirement is the development of the advanced coated fuel particles with use of ZrC instead of SiC. Although SiC has good properties, it gradually loses mechanical integrity at very high temperatures, above 1700°C, by thermal dissociation. Zirconium carbide (ZrC) is well known as a refractory and chemically stable compound, having a melting point of 3540°C. In addition, it has a higher resistance to the chemical attack by fission product elements such as Pd and appears to be a better barrier to Cs in post-irradiation heating experiments [1]. Therefore, the ZrC has been focused on replacing material of the SiC layer in the TRISO coating layers, and many researchers have been reported the ZrC coating methods with various Zr-salts-CH_4 as a source materials in the fluidized bed chemical vapor deposition (FBCVD) equipments [2-5].

For the fabrication of the ZrC TRISO coated particles by the FBCVD process, some Zr-salts, such as $ZrCl_4$, $ZrBr_4$ and ZrI_4 were used as source materials [2-5]. Among these processes, chloride process is reasonable process because of less hazardous and better stoichiometric composition than bromide and iodide process, respectively. Owing to nature of $ZrCl_4$, which sublimate about 260°C, the homogeneity of ZrC layer is degraded by the sweep effect which is caused by supplying carrier gas to transfer the $ZrCl_4$ vapor to the reactor. In this reason, various designs of vaporizers have been proposed to constantly supply the $ZrCl_4$ to the reactor for obtaining the homogeneous ZrC layer.

In this study, we manufactured the identical vaporizer to deposit the ZrC film in the LPCVD system, as a preliminary study of ZrC TRISO. The homogeneity of ZrC film was investigated with various conditions, vaporizer temperature and amount of $ZrCl_4$ at fixed temperature and system total pressure of deposing condition.

2. Experimental Procedure

The ZrC film was deposited on graphite substrate in the LPCVD system, and initial process conditions of ZrC deposition were defined by calculating the equilibrium mole fraction of ZrC with the input gas ratios and deposition temperatures in the different $ZrCl_4/CH_4/H_2$ systems by the SOLGASMIX-PV program. The calculated optimum deposition conditions were T=1400℃, P=10torr, input gas ratio ($\alpha = [H_2 / (CH_4+ZrCl_4)]$) of 5, and source gas ratio ($\beta = [Zr / (Zr+C)]$ in the input gas) of 0.8.

For the constantly supplying the $ZrCl_4$ vapor into the reactor, we used the internally designed vaporizer which is shown in Fig. 1. The vaporizer was composed three heating part and two vessels. Vaporizer was equipped with throttle valve for automatic control of input gas ratio and vaporizer total pressure.

Prior to deposition, TG-DTA analysis was carried with inert condition to investigate the available sublimation temperature which starts at 258°C. The vapor pressures of $ZrCl_4$ with temperature above 260°C were investigated to control the amount of gas flow rate of source and carrier gas. Under fixed reactor condition which were calculated by the SOLGASMIX-PV program with deposition time of 3h, ZrC deposition on the graphite substrate was carried with vaporizer temperature and charged $ZrCl_4$ powder were ranged from 260°C to 310°C and 9g to 20g, respectively.

The crystal structure of ZrC film was investigated by XRD. The microstructure of ZrC film was observed by SEM (JEOL, JSM5200), and the homogeneity of ZrC films were evaluated with EDS in the mode of line scanning.

Fig. 1. $ZrCl_4$ vaporizer.

3. Results and Discussion

Figure 2 shows the TG-DTA data, which analyzed with ramping rate of 1℃/min in the Ar atmosphere. It seems to be appeared to sublimate start at 258°C, and weight change rapidly decrease to 283°C with high exothermic heat flow. Thus, the temperature range from 258°C to 283°C are not proper to deposition because amount of vapor would not enough and reproductive amount of $ZrCl_4$ vapor. In this reason, the ZrC films, deposited with vaporizer temperature of 260°C and 270°C, were observed without uniformity in this study.

On the other hand, ZrC film, deposited with uniformity, was observed above the vaporizer temperature of 280°C. Thus, for the uniform coating, the vaporizer temperature

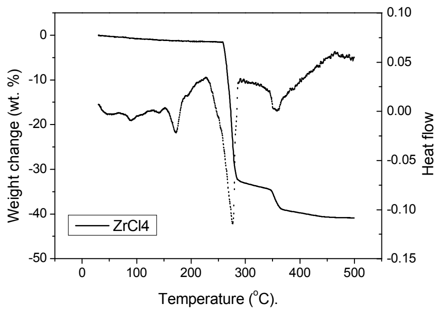

Fig. 2. TG-DTA result of $ZrCl_4$ powder.

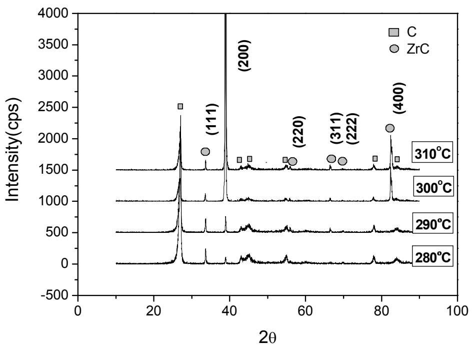

Fig. 3. XRD patterns of ZrC films with various vaporizer temperatures.

should be higher than 280°C.

Figure 3 shows that the XRD patterns with various vaporizer temperature above 280°C. The XRD spectra showed that all of ZrC films were corresponded to cubic ZrC in the JCPDS 35-0784. Some of ZrC films were highly oriented to the direction of (200) at higher vaporizer temperatures. In addition, the homogeneity of ZrC film was maintained at the vaporizer temperature of 300°C and 310°C. Though, the ZrC film was confirmed by XRD results at the vaporizer temperature of 280°C and 290°C, those of ZrC films were not had homogeneity as shown in Fig. 4, showing the EDS results in the mode of line scanning.

The thicknesses of ZrC films were 2.02, 4.02, 4.07 and 3.35μm with 10°C interval of vaporizer temperature of 280°C, respectively. The highest deposition rate was observed at 300°C with homogeneity. The vaporizer temperature of 280°C, the composition of Zr in the ZrC film was very small and decreased along the thickness of film, and heterogeneity of film near the surface also observed at 290°C, 300°C and 310°C, as shown in Fig. 4. As increasing the deposition time, depletion of $ZrCl_4$ would occur in the vaporizer. Thus, the larger amount of $ZrCl_4$ powder was needed to get the homogeneous film

Figure 5 shows the cross-sectional image and EDS result deposited with 20g of $ZrCl_4$ power and vaporizer

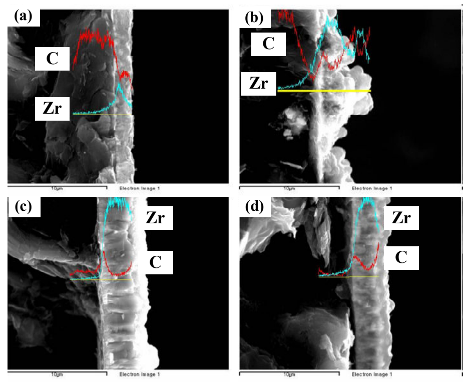

Fig. 4. EDS results of ZrC film with various vaporizer temperatures (a) 280, (b) 290, (c) 300, and (d) 310°C, respectively.

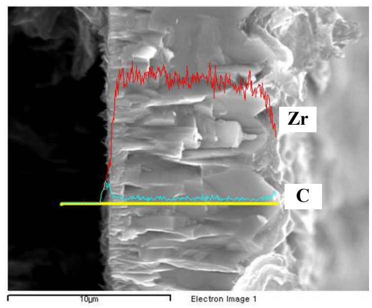

Fig. 5. EDS result of ZrC film with various vaporizer temperatures 300℃ and amount of $ZrCl_4$ powder of 20g.

temperature of 300°C. Homogeneity of film with thickness of 11.3μm was maintained to the surface of layer.

4. Conclusions

ZrC film was deposited at T=1400°C, P=10torr, and amount of $ZrCl_4$ powder of 9g on the graphite substrate. The vaporizer temperature was important parameters for the ZrC deposition. At the low vaporizer temperature, deposited ZrC film with heterogeneity. However, the high vaporizer temperature, highly oriented ZrC film was deposited with homogeneity, and the thickness of layer proportion to amount of $ZrCl_4$ powder.

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