

Fabrication and characterization of SiC and ZrC composite coating on TRISO coated particle

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1. Introduction

SiC coating is widely suggested as structural materials for nuclear application due to its excellent high irradiation resistance properties and high temperature mechanical properties[1,2]. SiC coating on TRISO structural-Isotropic (TRISO) coated fuel particles plays an important role as a protective layer from radioactive fission gas and a mechanical structural layer. TRISO coated fuel particles embedded in a carbonaceous matrix is considered as the fuel of high temperature gas-cooled reactors. The typical TRISO coated particles consist of a kernel, a buffer porous pyrolytic carbon (PyC) layer and an IPyC/SiC/OPyC trilayer. In the TRISO coated particle, SiC provides mechanical strength and retains fission products, due to its good high temperature strength, corrosion resistance and low neutron absorption cross-section. However, SiC has the limitation for high temperature application because of the active oxidation above 1650 °C[3]. ZrC is one of the most promising ceramics for ultrahigh temperature application due to the formation of a protective zirconia layer at high temperature[4,5] In this study, SiC and ZrC coating were deposited separately and SiC and ZrC composite coating were deposited on the TRISO coated particle via fluidized bed chemical vapor deposition (FBCVD) method. SiC and ZrC composite coating layer is considered to improve an oxidation resistance at high temperature. The microstructure and phase of composite coating layer were observed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), XRD, and Raman spectroscopy.

2. Methods and Results

TRISO coating layer was deposited on a spherical particle by a FBCVD method. The ZrO₂ spherical particles were used as a simulant kernel. TRISO coating layers consisting of a porous buffer layer, an inner PyC layer were sequentially deposited before depositing SiC or ZrC coating layer. SiC coating layer was deposited using the MTS (Methyltrichlorosilane: CH₃SiCl₃), ZrC coating layer was deposited using ZrCl₄ and CH₄. Since the ZrCl₄ source material is in a solid state at room temperature, a sublimation system was installed to vaporize the source material. The flow rate of the ZrCl₄ gas was controlled by the pressure of the vaporizer, the flow rate of Ar as a carrier gas, and the sublimation

temperature. The screw feeder system of a source material was introduced to supply the source material uniformly. The detail deposition process of SiC and ZrC coating on TRISO was explained in other paper[6,7]. SiC and ZrC composite coating layer of different microstructure were prepared by adjusting the gas flow rate of MTS, ZrCl₄ and CH₄. The microstructure of SiC and ZrC composite coating was observed using SEM and TEM. TEM specimens were taken at the center of the coating layer using a focused ion beam (FIB) technique.

Table 1. The deposition condition of SiC, ZrC, SiC and ZrC composite coating layer.

Coating	Q	ZrCl ₄	CH ₄	MTS	Ar(D)	H ₂ (D)	Ar(C)	H ₂ (C)
SiC	3000			30	1480	1110		380
ZrC	3972	95	31		1582	1923	341	
SiC/ZrC_1	3925	40	10	30	1581	1543	341	380
SiC/ZrC_2	4000	100	25	30	1581	1543	341	380

Fig.1 shows the each coating layer of SiC, ZrC and SiC and ZrC composite. The deposition condition of each coating layer was shown in Table 1. The deposition temperature of all coating was 1500 °C and ZrCl₄ source gas sublimation temperature was 400 °C. Two different SiC and ZrC composite coating were coated on one spherical particle. Each coating layer has the thickness of 20 ~ 30 μm and well deposited on inner PyC layer.

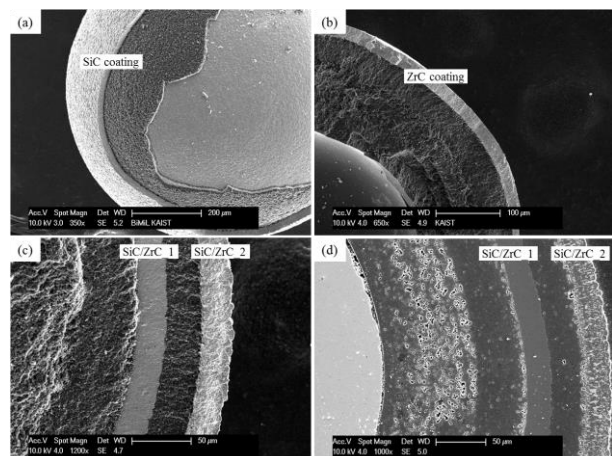


Fig. 1. Fracture surface of (a) SiC coating layer, (b) ZrC coating layer, and (c) SiC and ZrC composite coating layer. (d) Polished surface of SiC and ZrC composite coating layer.

Fig. 2 shows XRD results of SiC, ZrC coating and SiC/ZrC_2 coating. SiC and ZrC coating show its own XRD pattern. From the results of SiC/ZrC_2 coating XRD pattern, it is observed that SiC and ZrC composite coating was successfully deposited with the deposition condition. XRD analysis of the SiC/ZrC_1 specimen couldn't be conducted because the coating layer is located in inside of TRISO coating layer. We have a plan to measure XRD of SiC/ZrC_1 specimen after fabricating the SiC/ZrC_1 coating in outside layer in a later study.

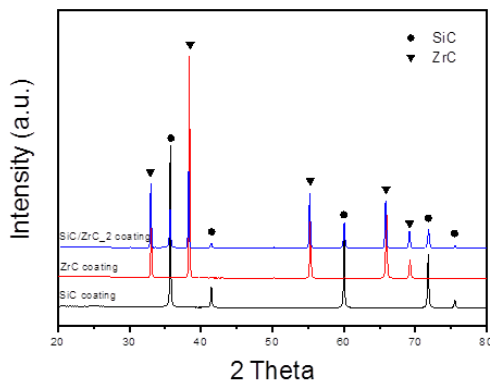


Fig. 2. XRD results of SiC coating, ZrC coating, and SiC/ZrC_2 coating.

In order to investigate the phase of each composite coating layer, Raman analysis was conducted. Fig. 3 shows the Raman spectroscopy results of SiC/ZrC_1 and SiC/ZrC_2 coating. In the result of SiC/ZrC_1 coating (fig. 3(a)), transverse and longitudinal peak of SiC phase was observed. D-peak and G-peak of graphite related to carbon phase were also observed. From the Raman analysis of SiC/ZrC_1 coating, the coating consists of SiC main phase. There is possibility to exist free carbon or graphite related to carbon phase in the coating. In the results of SiC/ZrC_2 (fig. 3(b)), black area shows SiC peak, and white area shows weak SiC peak and various carbon related peak. It can be known that white area means ZrC phase compared to the XRD results. Generally, it is very hard to obtain stoichiometry ZrC coating by CVD[8,9]. Carbon vacancy induced or graphite related to carbon phase induced peak in Raman spectra were usually observed in CVD-ZrC coating[10]. In the ZrC phase of ZrC/SiC_2 coating, carbon vacancy induced peak such as acoustic branches of A1 and A2, Optical branches of O1 and O2 was observed. Free carbon or graphite related to carbon phase peak was also observed. This means that non-stoichiometry ZrC phase and free carbon co-existed in the ZrC/SiC_2 coating layer.

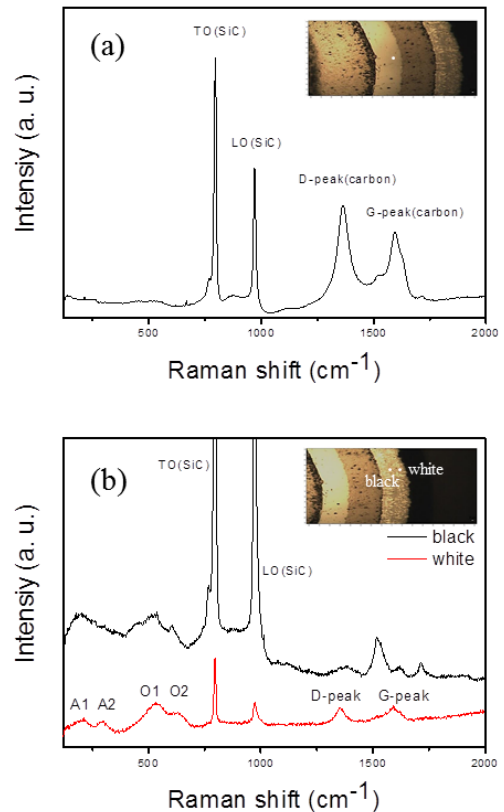


Fig. 3. Raman spectra of (a) ZrC/SiC_1 coating and (b) ZrC/SiC_2 coating.

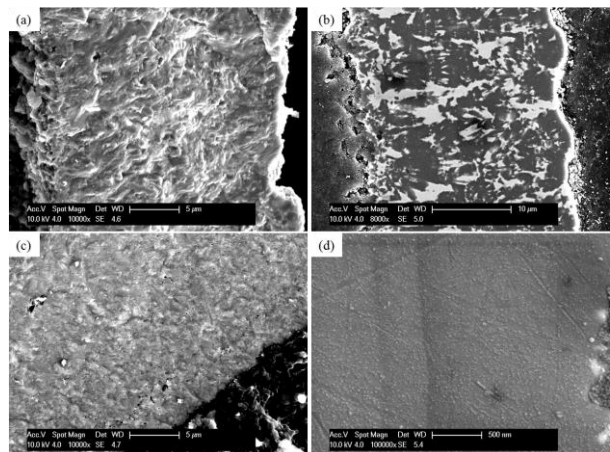


Fig. 4. The fracture and the polished surface micrograph of (a),(b) SiC/ZrC_2 coating, (c),(d) SiC/ZrC_1 coating.

Fig. 4 shows the fracture and the polished surface micrograph of SiC and ZrC composite coating. In the polished surface micrograph of SiC/ZrC_2 (fig. 4(b)), two phases of SiC and ZrC were clearly observed and separated. From the EDS analysis, it is confirmed that white phases are ZrC phase and gray phases are SiC phase. Fig. 5 shows high resolution TEM image of boundary between SiC and ZrC phase. Clean grain boundary between SiC and ZrC phase was observed.

There was no composite phase of Zr and Si in grain boundary. In the fracture surface micrograph of SiC/ZrC_1 (fig. 4(c)), the coating layer shows low quality and have many small pores. In the high magnification micrograph of polished surface of the coating, many small particles size of 10 ~ 20 nm was observed in the surface of the coating. These tiny particles were observed in entire coating surface uniformly. The detail and additional analysis is necessary as to whether the some particles are actually present inside the coating.

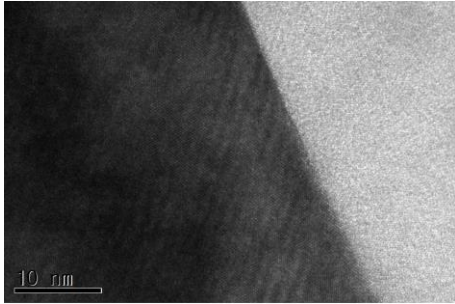


Fig. 5. High resolution TEM image of boundary between SiC and ZrC

3. Conclusions

SiC, ZrC coating and SiC/ZrC composite coating on spherical particle were successfully deposited via FBCVD method by adjusting source gas flow rate. In the SiC and ZrC composite coating, SiC phase and ZrC phase were observed by XRD and SEM analysis. In the condition of 100 sccm of ZrCl₄, 25 sccm of CH₄, and 30 sccm of MTS, only two phases of SiC and ZrC were observed and two phases are located with clean grain boundary. In the condition of 40 sccm of ZrCl₄, 10 sccm of CH₄, and 30 sccm of MTS, SiC coating is mainly deposited and many tiny particles were observed inside the coating. An additional analysis is needed to confirm that the particles are actually present.

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