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Fabrication and structural stability of ZrC-SiC double layer TRISO coated particles

H. -G. Lee*, S. H. Lee, D. J. Kim, J. Y. Park, W. –J. Kim
Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, Korea
**Corresponding author: hglee@kaeri.re.kr*

1. Introduction

TRISO coated fuel particle is suggested as fuel of high temperature gas-cooled reactors. A TRISO coated particle is composed of four layers of buffer PyC, inner PyC, SiC and outer PyC layer coated on UO_2 kernel. SiC coating layer, which is a structural layer, maintain the structural integrity of nuclear fuel particle at high temperature and retains fission products since its excellent mechanical properties at high temperature and good irradiation resistance. However, β-SiC coated by CVD causes a phase change to α-SiC above 1800 °C, which may cause damage to the TRISO coating layer. Since the SiC layer reacts with the fission product Pd to form Pd_2Si at high temperature, which causes corrosion, resulting in a loss of ^{137}Cs trapping ability of TRISO coated fuel particle[1,2].

ZrC is an advanced ceramic material that is more stable than SiC at high temperatures due to its high melting point[3,4]. ZrC is thermally stable with no phase transition up to 2850 ℃, has excellent corrosion resistance to Pd, and excellent radiation resistance. ZrC coating has a low diffusion coefficient for Pd and Cs at high temperatures, which makes it easy to prevent release of fission products. ZrC coating has been studied as a structural layer of TRISO coated fuel particles. The CVD-coated ZrC layer is difficult to fabricate by precisely controlling the stoichiometry so that defects such as free carbon and carbon vacancy are easily formed in the coating layer, which is likely to cause deterioration of mechanical properties[5,6]. The CVD ZrC coating layer has a low high temperature strength, which makes it difficult to guarantee the structural integrity of TRISO coated fuel particles.[7]

In this study, ZrC-SiC double coating layer was proposed as a structural layer of TRISO coated particles to compensate for disadvantages of SiC and ZrC coating. The ZrC-SiC double coating layer should be fabricated with a ZrC coating layer on the IPyC layer and a SiC coating layer coated continuously on the ZrC coating layer. Using the FBCVD, ZrC and SiC layers were continuously coated to fabricate ZrC-SiC double layer TRISO coated particle. ZrC and SiC coating layers show different thermal expansion coefficients, so structural integrity must be confirmed. The soundness and mechanical properties of the double coating layer was evaluated after heat treatment at high temperature.

2. Methods and Results

TRISO coated article was produced by a FBCVD (Fluidized –Bed Chemical Vapor Deposition) method. The ZrO_2 spherical particles were used as a simulant kernel. ZrC and SiC coating layer were continuously deposited on the IPyC layer. ZrC coating was deposited from $ZrCl_4$, CH_4, H_2 and Ar at 1500 °C, $ZrCl_4$ powder were vaporized at 290 °C ~ 305 °C in the sublimation chamber and supplied into the reactor with an Ar carrier gas. The stoichiometry of the ZrC coating was controlled by the supply amount of the Zr source which was adjusted by the sublimation temperature of $ZrCl_4$. The screw feeder supply system was applied to deposit uniformly entire coating and to prevent the condensation of $ZrCl_4$ powder. The ratio of source gases and the ratio of dilution gases were 0.8 and 0.5 respectively. SiC coating was deposited from MTS (Methyltrichlorosilane), H_2, and Ar. The detail deposition process of Zrc coating and SiC coating on TRISO was explained in other paper[8,9].

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

Coating	Q	CH_4	MTS	Ar(D)	H_2(D)	Ar(C)	H_2(C)	$ZrCl_4$ sublime. T.
SiC	3000		30	1480	1110		380	
ZrC1+x	3972	31		1582	1923	341		290
$ZrC1_{1\pm\Delta}$	3925	10	30	1581	1543	341	380	305

Fig. 1 show cross-section OM images of the two kinds of ZrC-SiC double layer TRISO coated particles and raman spectroscopy results of ZrC coating of each ZrC-SiC double layer. The deposition condition of each coating layer was shown in Table 1. Fig. 1 (a), (c) show ZrC coating with excess free carbon, which has the stoichiometry of ZrC_{1+x}. Fig. 1 (b), (d) shows ZrC coating with almost same ratio of stoichiometry. In the raman spectroscopy result of ZrC_{1+x} coating, D-peak and G-peak of graphite related to carbon phase were observed. In the raman spectroscopy analysis of $ZrC_{1\pm\Delta}$ coating, a very small D-peak and G-peak and a broad small peak around 600 cm^{-1} was observed. Carbon vacancy induced peak with optical branches of O1 and O2 observed 540 and 600 cm^{-1}[10]. From the microstructure and the raman anlaysis, it was confirmed that ZrC-SiC double layer TRISO coated particles were successfully fabricated with various stoichiometry of ZrC coating.

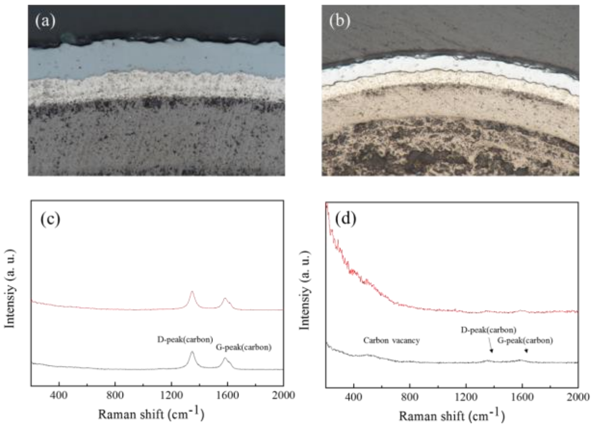

Fig. 1. OM images of ZrC-SiC double layer TRISO coating and raman spectroscopy of ZrC coating of each double layer coating. (a),(c) ZrC_{1+x}-SiC double layer, (b), (d) $ZrC_{1\pm\Delta}$-SiC double layer.

The thermal expansion coefficients of SiC coating and ZrC coating are 4.0 ~ 4.8 x 10^{-6} K^{-1} and 6.6 ~ 6.8 10^{-6} K^{-1}, respectively. The thermal expansion coefficient of ZrC coating is about 50% larger than that of SiC coating. SiC-ZrC double layer TRISO particles were heat-treated at high temperature to confirm the integrity of the SiC and ZrC coating layers. Two kinds of SiC-ZrC double layer TRISO coated particles were mounted and then the half of the spherical shape was polished. Then, the mounting resin was removed to fabricate a hemispherical SiC-ZrC double layer TRISO coating. These specimens were heat treated at 1800 °C for 2 hours. After annealing, OM and SEM images of the hemispherical SiC-ZrC double layer TRISO coated particle are shown in Fig. 2 No peeling of two coating layers was found due to the difference in thermal expansion coefficient, and each coating layer was confirmed to be sound without causing any breakage.

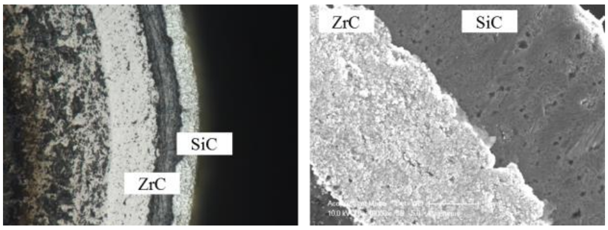

Fig. 2. OM and SEM images of the hemispherical SiC-ZrC double layer TRISO after heat treatment at 1800 °C

The interface between ZrC coating and SiC coating of annealed SiC-ZrC double layer TRISO coated particles was analyzed in detail through TEM. Fig. 3 (a) shows the SiC-ZrC interface TEM result of the ZrC_{1+x}-SiC double layer coating. From the TEM analysis, the existence of free carbon between each ZrC grain was observed in the ZrC coating. This result agrees with the raman analysis result. Due to the large amount of free carbon, free carbon are mostly present at ZrC and SiC interfaces. ZrC, SiC,and free carbon were found to be bonded at the interface without any other phase. Fig. 3 (b) shows the SiC-ZrC interface TEM result of the $ZrC_{1\pm\Delta}$-SiC double layer coating. ZrC and SiC grains are in direct contact with each other and are well bonded without any amorphous phase or defect in the interface.

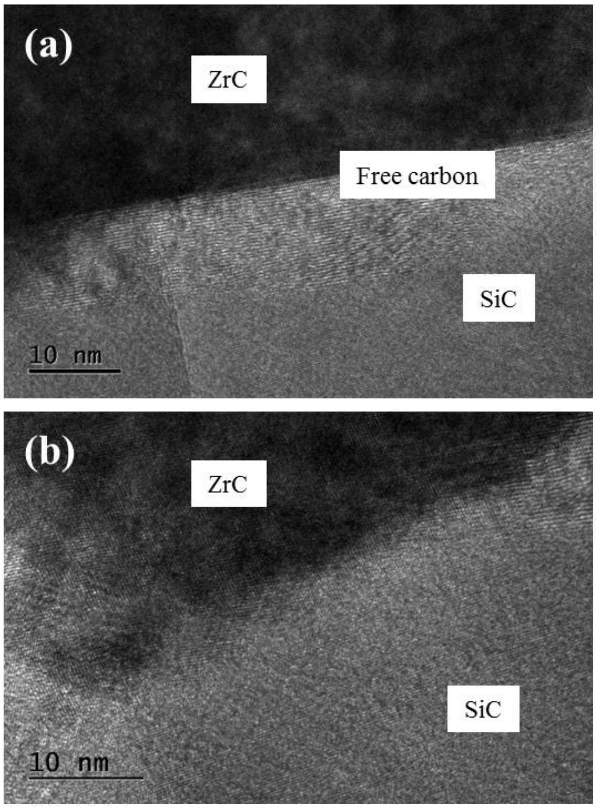

Fig. 3. TEM micrograph images of the interface between ZrC and SiC of (a) ZrC_{1+x}-SiC double layer coating, (b) $ZrC_{1\pm\Delta}$-SiC double layer coating

3. Conclusions

SiC-ZrC double layer TRISO coated particles were successfully fabricated by continuously process using FBCVD method. Two type of ZrC coating which has different stoichiometry were deposited by adjusting Zr source. After annealing at 1800 ° C for 2hr, the ZrC-SiC double layer coating maintained its structural integrity and did not cause peeling or breakage of the coating. In the ZrC_{1+x}-SiC double layer coating, the free carbon was mostly present between the interface of ZrC and SiC interfaces. In the $ZrC_{1\pm\Delta}$-SiC double layer coating, ZrC and SiC were in direct contact.

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