

Fabrication and Mechanical Properties Evaluation of Various Stoichiometry ZrC Coatings on TRISO Particles

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1. Introduction

TRISO coated fuel particle is developed for using nuclear fuel for HTGR(High Temperature Gas-cooled Reactor). TRISO coating layer is generally composed of four layer of buffer PyC layer, inner PyC layer, SiC layer, and outer PyC layer. SiC layer maintains the structural integrity of TRISO coated fuel particle at high temperature and retains fission products. SiC layer has excellent mechanical properties at high temperature but also has some problem at high temperature. β -SiC deposited by CVD method cause a phase change to α -SiC above 1800 °C, which may cause damage to the coating layer. Since the SiC layer reacts with the fission product Pd to form Pd₂Si, which causes corrosion, resulting in a loss of ¹³⁷Cs trapping ability of TRISO coated fuel particle[1,2]

ZrC coating layer, which is high temperature ceramics, has been proposed as an alternative coating layer due to its low reactivity with fission products and high temperature stability. ZrC has excellent corrosion resistance against Pd so that the coated particles are not broken at 2400 °C[3,4]. However, ZrC coating is difficult to fabricate with a Zr/C stoichiometric ratio of 1:1 because ZrC is thermodynamically more likely to form ZrC+C or Zr_{1+x}C than pure ZrC. The free carbon or carbon vacancy within ZrC coating reduces the mechanical and radiation resistance of the ZrC coating [5,6]. In this study, various stoichiometry ZrC coatings were fabricated by two kinds of source gas supply method. The elastic modulus and the hardness using nanoindentation, and the fracture strength using a crush test were measured according to the stoichiometry of ZrC.

2. Methods and Results

2.1 Fabrication of various stoichiometry ZrC coating

The ZrC coating layers were deposited by fluidized-bed CVD equipment with a vaporizing system. ZrCl₄ powder which is used as a source material is vaporized in a vaporizing system and vaporized ZrCl₄ gas is supplied to reaction furnace with a carrier gas. A flow rate control of ZrCl₄ source gas uses two methods: a sublimation temperature control and a source powder supply amounts control. ZrC coatings were deposited at 1500 °C through the reaction between ZrCl₄ gas and CH₄ gas.

Fig. 1 shows the Raman spectroscopy of ZrC coatings which is fabricated with a sublimation temperature control method. The ZrCl₄ powder sublimation temperature of ZTR-1, 2, 3 sample in vaporizing system were 300 °C, 290 °C, and 280 °C, respectively.

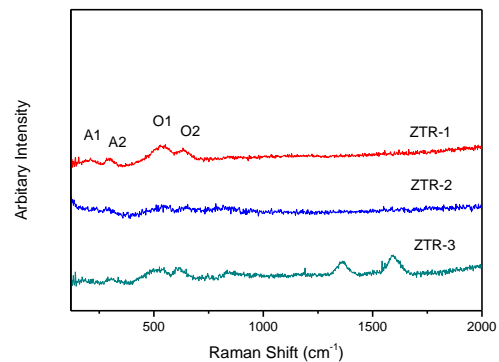


Fig. 1 Raman spectra of the ZrC coatings fabricated with a sublimation temperature control method.

As the sublimation temperature decreases, amounts of Zr source gas supplied decreases. ZTR-1 sample shows carbon vacancy peak, which present acoustic branches at about A1 = 210 cm⁻¹, A2 = 280 cm⁻¹ and optical branches at about 540 cm⁻¹ and 600 cm⁻¹ due to sufficient Zr gas supply. ZTR-3 sample shows two peaks induced by free carbon due to the lack of Zr gas supply.

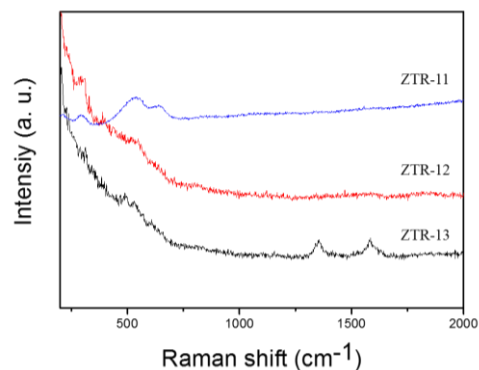


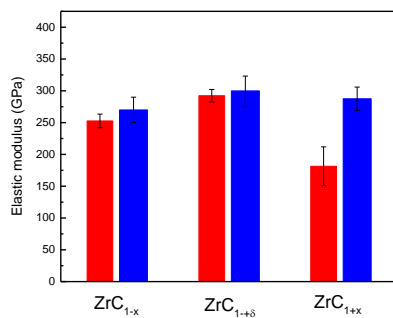
Fig. 2 Raman spectra of the ZrC coatings fabricated with a source powder supply amounts control method.

Fig. 2 shows Raman spectroscopy of ZrC coatings which is fabricated with a source powder supply amounts control. Using the screw feeder, ZrCl₄ powder was supplied into the vaporizing system. ZTR-11 sample with a high supply of ZrCl₄ powder shows

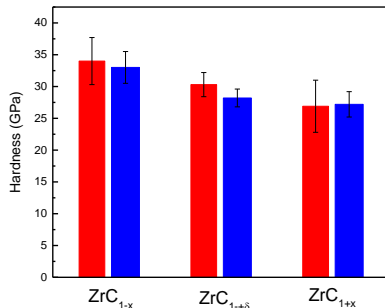
carbon vacancy related peaks, ZTR-13 sample with a low supply of $ZrCl_4$ powder shows free carbon peaks. ZTR-2 sample and ZTR-12 sample were deposited with a Zr/C stoichiometric ratio of 1:1 from both two methods in which carbon vacancy related peaks and free carbon peaks were not observed.

2.2 Mechanical properties of various stoichiometry ZrC coating

The mechanical properties of deposited ZrC coatings with various stoichiometry were measured. The elastic modulus and the hardness of ZrC coating were measured using nanoindentation. 27 points for each coating conditions were tested.



(a)



(b)

Fig. 3. The mechanical properties of various stoichiometry ZrC coatings. (a) elastic modulus, (b) hardness

Fig. 3 shows the elastic modulus and the hardness values of various stoichiometry ZrC coatings. The red one indicates the coatings fabricated with a sublimation temperature control method and the blue one indicates the coatings fabricated with a source powder supply amounts control method. In the ZrC_{1+x} coating with free carbon, the hardness was the lowest, and the hardness was slightly increased in the ZrC coating with a Zr/C stoichiometric ratio of 1:1. In ZrC_{1-x} coating with carbon vacancy, hardness was the highest. This result shows a similar tendency to that of Ogawa and He measured by the Vickers and Knoop method according to the C/Zr ratio [7,8]. In the results of He et al., when

the content of carbon vacancies increases, the hardness of the ZrC coating layer increases and shows the highest value, and then decreases. When the amount of free carbon increased, the hardness of the ZrC coating layer decreased. The ZrC_{1-x} coating layer prepared in this study is thought to have an increased hardness value because it contains less carbon vacancies.

Table 1 shows the fracture strength of the ZrC coating measured by a crush test. Fracture strength measurement method by a crush test was shown in our previous report[9]. 20 samples were tested for each coating. All ZrC coatings show high fracture strength value above 1300 MPa, which is sufficiently high value compared to the crush strength of SiC coating of 1057 MPa[10].

Table 1. Crush test results of various stoichiometry ZrC coatings.

	ZrC-1	ZrC-2	ZrC-3
Weibull modulus	4.71	3.05	4.36
Weibull characteristic value	7.91	5.78	7.94
Thickness of coating layer, mm	19.33	33.91	13.24
Strength of coating (Prediction), MPa	2422	1313	1926

3. Conclusions

The various stoichiometry ZrC coatings were fabricated by fluidized-bed CVD methods with two $ZrCl_4$ supply methods: a sublimation temperature control method and a powder supply amount control method. ZrC coatings with uniform stoichiometry were prepared through all two $ZrCl_4$ supply methods. The stoichiometry of ZrC coatings were confirmed by Raman analysis. The elastic modulus and hardness of the ZrC coating layer were measured using nanoindentation. The mechanical properties of the ZrC_{1+x} coating layer with free carbon were the lowest, and the mechanical properties of the ZrC_{1-x} coating layer with carbon vacancies were the highest. The fracture strength of the ZrC coating was observed through the crush test. The fracture strength of the ZrC coating on the ZrC-TRISO particle revealed sufficiently high value.

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