Development of security and safety fuel for Pu-burner HTGR - Test and characterization for ZrC coating -

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Abstract

To develop Pu-burner high temperature gas-cooled reactor (HTGR) attaining very high burn-up around 500 GWd/t, the security and safety fuel (3S-TRISO fuel) is proposed. The 3S-TRISO fuel employs the coated fuel particle with a fuel kernel made of plutonium dioxide (PuO_2) and yttria stabilized zirconia (YSZ) as an inert matrix. Especially, a zirconium carbide (ZrC) coating is one of key technologies of the 3S-TRISO, which performs as an oxygen getter to reduce the fuel failure due to internal pressure during the irradiation. R&Ds on ZrC coating directly on the dummy kernel made of YSZ which surrogates PuO_2 -YSZ have been started in the Japanese fiscal year 2015. As results of ZrC coating tests on YSZ particle by the bromide process developed in Japan Atomic Energy Agency, stoichiometric ZrC coatings with 18 - 21 μm of thicknesses were obtained with 0.1 kg of particle loading weight. As indicated by a thermochemical analysis on the chemical stability of YSZ against the ZrC bromide process, no deterioration of YSZ exposed by source gases of ZrC bromide process was observed through the characterization by Scanning Transmission Electron Microscope (STEM) observation. Finally, reproducibility of stoichiometric ZrC coating on YSZ particle was demonstrated by the bromide chemical vapor deposition process.

Keywords : Coated fuel particle, Zirconium carbide, Chemical vapor deposition, Coating process, Characterization

1. Introduction

A concept of a plutonium burner HTGR named as Clean Burn, which has a high nuclear proliferation resistance, had been proposed by Japan Atomic Energy Agency (Goto, et al., 2015). In the Clean Burn concept, the coated fuel particle which consists of the microsphere of yttria-stabilized zirconia (YSZ) containing PuO_2 with tri-isotropic (TRISO) coating is employed in addition to the high nuclear proliferation resistance. Furthermore, very high burn-up around 500 GWd/t is required to incinerate a large amount of fissile plutonium efficiently with once through (Fukaya, et al., 2014). Under such an extremely high burnup targeted for Pu-burner HTGR, carbon monoxide (CO) and fission gases generating by fission cause to fail very thin ceramics (in order of 10 μm) coating layers of the coated fuel particle such as silicon carbide (SiC) and pyrolytic carbon (PyC) due to the internal pressure increase dominantly. Therefore, we propose to introduce PuO_2 -YSZ TRISO fuel with zirconium carbide (ZrC) coating, named the security and safety fuel (3S-TRISO fuel), to the Clean Burn to enhance its safety under high burnup (Goto, et al., 2015).

ZrC is known as an advanced coating material for the coated fuel particle having higher temperature resistance and higher chemical stability against metallic fission products (FPs) than those of the conventional SiC (Ogawa, et al., 1992, Minato, et al., 1997). In the past, for taking advantage of ZrC's excellent properties alternative to SiC, JAEA performed R&D on ZrC coating by chemical vapor deposition (CVD) using fluidizing bed coater. Then, it is important to control the stoichiometry of ZrC (i.e., of which the carbon to zirconium ratio is 1) with regards to thermal properties and performance on retentiveness against FPs (Ueta, et al., 2008). On the other hand, ZrC is easily oxidized to be zirconium

dioxide (ZrO_2) under high temperature and oxidizing condition (Ueta, et al., 2008). For the 3S-TRISO fuel, ZrC is coated directly on plutonium dioxide (PuO_2) fuel kernel including yttria stabilized zirconia (YSZ) as the inert matrix to act as an oxygen getter, which reduces generating CO gas to prevent the coated fuel particle from failure due to its internal pressure.

Consequently, JAEA had succeeded in the stoichiometric ZrC coating on the pyrolytic carbon (PyC)-coated microspheres with 0.78 mm of diameter which surrogated the coated fuel particle for the HTTR (Ueta, et al., 2008). On the other hand, in the preliminary estimation on failure of the 3S-TRISO fuel due to internal pressure increase, diameter of the fuel kernel was estimated at 0.3 – 0.5 mm which is smaller than that of the HTTR fuel (Goto, et al., 2017). Then, in this study, the diameter of the kernel to coat ZrC directly shall be at least 0.2 mm smaller than that in the previous. The fluidizing condition depends not only on the diameter of the kernels to be coated but also coating temperature, flow rate of mixed source gases, etc., which should be optimized for conducting the ZrC coating. Hence, ZrC coating on the smaller kernel is one of key technologies to establish the 3S-TRISO fuel fabrication technologies.

The establishment of the technology of coating ZrC layer on the smaller kernel is conducted by the following 3 steps, the first two steps in Japanese fiscal year (JFY) 2016 and the last in JFY 2017;

- ZrC coating test directly on the bare YSZ dummy kernel with 0.7 mm of diameter is conducted to confirm applicability of coating condition for the stoichiometric ZrC obtained in the previous study.
- Preliminary fluidizing test with smaller YSZ dummy kernel with 0.4 mm in diameter is conducted to optimize fluidizing condition.
- ZrC coating test on cerium dioxide (CeO_2)-YSZ kernel surrogating PuO_2 -YSZ with 0.4mm of diameter (Saiki, et al., 2017) is conducted with the optimized gas flow rate.

This paper describes interim results in JFY 2016 on coating test and characterization of ZrC coating on YSZ dummy kernel for 3S-TRISO fuel for Pu-burner HTGR.

2. Experimental

2.1 ZrC coating condition by the bromide process

For ZrC coating, the bromide process was applied, which was originally developed in JAEA to produce a stoichiometric composition of ZrC (Ogawa, et al., 1981). In this process, the ZrC-coating layer is deposited with pyrolytic reaction of zirconium bromides (ZrBr_x ; ZrBr_4 is dominant), CH_4 and H_2 at 1300 to 1500 °C in a fluidized bed. Following equations describe the main reactions of the bromide process, in which solid and gas phases are expressed in parentheses and square brackets, respectively;

In this study, a large-scale ZrC coater with capacity of 0.2 kg batch size was used as shown in Fig. 1. (Ueta, et al., 2008)

Fig.1 ZrC coater constructed in JAEA Oarai.

Liquid bromine is vaporized with argon as carrier gas at a temperature of 0 °C, and the produced bromine gas reacts with metallic zirconium sponge loaded in the coater, and then produces ZrBr_x gases at about 600 °C. A gas mixture of ZrBr_x gases, methane and hydrogen is transferred into the coater having a particle fluidizing bed, and ZrC is coated on the surface of the particle.

For the coating conditions of the stoichiometric ZrC, deposition temperature was determined in the basis of precursor research (Ueta, et al., 2008). Figure 2 shows a relationship between stoichiometry, efficiency of source gas reaction, pyrolysis of CH_4 or conversion of ZrBr_4 to produce ZrC, as a function of coating temperature. In the figure, efficiency of conversion of ZrBr_4 bears a proportionate relationship to coating temperature. According to this result, coating temperature at 1350 °C was selected to react the stoichiometric ZrC, in which the molecular rates of ZrBr_4 and methane contributing to be $\text{ZrC}_{1.0}$ are about 59 - 63% and 43 - 46%, respectively. Based on the above, this study adopted flow rates of bromine with argon career and methane gases at 1.5 L/min (corresponding to about 0.003mol/min of ZrBr_4 , which assumes that 100% of bromine gas vaporizing at 9 kPa of partial pressure at 0°C reacts with zirconium) and 0.1 L/min (about 0.004mol/min), respectively.

Fig. 2 Relationship between ZrC stoichiometry, efficiency of source gas reaction as a function of coating temperature. The number in parentheses means ZrC stoichiometry.

2.2 Preliminary fluidizing test with YSZ particles

To determine flow rates of argon and hydrogen gases to make stable fluidization of the particle, the preliminary tests were carried out. Dummy particles with diameters of 700 and 400 μm made of YSZ were purchased from Nikkato Cooperation. Weight of particle loading per 1 batch was settled at 0.1 kg. For tests with 0.7mm YSZ particle, a fluidizing bed (42 mm in inner diameter, 60° of aperture angle) with single nozzle (3mm inner diameter) was applied for the ZrC coater. For tests with 0.4mm YSZ particle, new fluidizing bed (having same inner diameter and aperture angle as the single nozzle type) with 4 multi nozzle (1.5 mm of inner diameter for each) was applied to prevent the particle from dropping through nozzles. As the results of fluidizing tests using each bed, each diameter of particle with 0.1kg of batch size at 1350 °C, flow rates of source gases for stable fluidizing were determined; 4 to 6 L/min for hydrogen, and 8 L/min in total of hydrogen and argon mixed gas for both size of YSZ particle.

2.3 Inspections of ZrC coating

For the inspection of ZrC coating, the thickness of ZrC was measured by projector, and the mean value of ZrC coating thickness was evaluated with 50 particles sampled from each coating batch. To measure ZrC stoichiometry and density of ZrC coated on YSZ substrate, so-called the burn method was applied. In this method, YSZ substrate assumes to be changed in neither weight nor volume before and after the treatment. At the first step of this method, 3 samples (4 grams per 1 sample) of as-fabricated ZrC coated YSZ particle are picked up, and its volume (V_{ap}) and weight (W_{ap}) for each sample are measured by pycnometer and balance, respectively. At the second, samples are burned in air at 850 °C for 3 hours, then only ZrC is oxidized to be ZrO_2 powder. After dividing the burned YSZ dummy kernel from the burned coating, weights of the kernel (W_{bk}) and the coating (W_{bc}), and volume of kernel (V_{bk}) are measured by same way as the first step. Stoichiometric ratio (C/Zr) and density (ρ_{ZrC}) of ZrC coating layer can be calculated the following equations, in which M_{Zr} , M_C and M_{O_2} are masses of Zr atom (91.22), C atom (12.01) and O_2 molecule (32),

respectively:

$$\rho_{ZrC} = \frac{W_{ap} - W_{bk}}{V_{ap} - V_{bk}} \quad (6)$$

$$C/Zr = \frac{\frac{(W_{ap} - W_{bp}) \times (M_{Zr} + M_{O_2})}{W_{bc}} - M_{Zr}}{M_c} \quad (7)$$

In addition, scanning transmission electron microscopy (STEM) observation was carried out to characterize boundary between ZrC and YSZ. The specimen was treated by the focused ion beam (FIB) before the observation. HD-2700 Cs-STEM by Hitachi High-Technologies Corporation was used for the observation at 200kV of accelerated voltage under room temperature.

3. Results and discussion

3.1 ZrC coating on 0.7mm YSZ dummy kernel

The target thicknesses of ZrC coating layer on 700 μm particle was 20 μm . A differential pressure at the nozzle of fluidizing bed increases during the coating process because the coated particles become heavier while being coated with ZrC. Therefore, the coating duration of 60 - 90 minutes was selected to adjust the increase in differential pressure.

It is known that coating temperature is very sensitive to produce the stoichiometric ZrC (Ueta, et al., 2008). It is presumed that the circumferential stripes are created by cyclic change of pyrolytic efficiency of CH_4 due to the temperature oscillation during the coating, which brings on excess carbon generation (Ueta, et al., 2008). Also, it is known that content of carbon is relatively higher than that of zirconium at the dark layered contrasts by the EDX spectrum measurement (Ueta, et al., 2008). The free carbon segregation areas in ZrC coating should be eliminated from the viewpoint of the irradiation properties, since the retention of metal fission products by the ZrC including free carbon is rather poor, presumably owing to a diffusion path through the free carbon phase (Fukuda, et al., 1979). Therefore, in this study, coating temperature was controlled carefully to be stable at 1350 $^{\circ}\text{C}$ during the coating process to obtain uniform ZrC.

As results of ZrC coating test on YSZ dummy kernel with temperature at 1350 $^{\circ}\text{C}$, ZrC coating layers with 18 - 21 μm of thicknesses have been successfully obtained as shown in Figs. 3 and 4. Then, coating rate of ZrC during the test was 0.20 – 0.23 micron per a minute.

Fig. 3 Appearance of ZrC coated on YSZ particles.

Fig. 4 Cross section of ZrC coated on YSZ particle.

The measurement of ZrC stoichiometry, i.e., C/Zr ratio, resulted in 0.94 with high accuracy in the order of 0.01, which was a slightly lower figure than the stoichiometric ZrC (1.0). The density of the ZrC coating layer was measured as approximately 6.63 g/cm^3 , which corresponds to about 98% of the theoretical density (6.73 g/cm^3 by Kosolapova (1971)).

3.2 Characterization at ZrC and YSZ boundary

By the STEM observation, the dark-layered structures were observed in high angle annular dark field (HAADF). To evaluate influence of ZrC's stoichiometry in microscopic morphology at ZrC/YSZ boundary, two samples having different C/Zr ratios were supplied for STEM analysis. As the result, HAADF images are shown in Fig. 5.

In Fig. 5a, ZrC coating looks to be bonded on YSZ dummy kernel, although some pores appear to exist due to the lack of crystal at the boundary of them. On the other hand, it was indicated that the high-dense regions designated, and the low-dense regions were layered with a relation to the deposition direction. It was seen that the dark layered contrasts were distributed non-uniformly. It was suggested that the low-dense region would be the area of segregated excess free carbon as identified in the precursor research (Ueta, et al., 2008). On the other hand, in these figures, polygonal-shaped pores are observed in both YSZ kernel and ZrC coating.

As one of the reasons on generation of pores at YSZ/ZrC boundary, the possibility of the reaction of ZrC source gas such as Zr bromide with YSZ is suggested. Therefore, thermochemical equilibrium analysis on the ZrC bromide process with YSZ base material was carried out. FactSage5.5 (CRCT, 2018) is used for the calculation. The calculation condition is assumed as followings; YSZ base material consisting of $10\% \text{ Y}_2\text{O}_3 + 90\% \text{ ZrO}_2$ (1 mol), source gases consisting of $\text{ZrBr}_4 + \text{CH}_4 + \text{H}_2$ (10 : 10 : 1600 mol, respectively) at $1,000 - 1,600^\circ\text{C}$ of coating temperatures at 1 atom of atmosphere.

Fig. 5 HAADF images of YSZ/ZrC boundaries (C/Zr ratio: 1.30 for a, 0.99 for b).

Figure 6 shows molecules of products as a function of coating temperatures by thermochemical equilibrium analysis. Although by-productions such as ZrBr_x ($x=2,3$), Br_x ($x=1,2$), H_2O and HBr are seen, almost no decrease of ZrO_2 , which is main composition of YSZ, was shown in the bromide process. Hence, it is suggested that YSZ would not be decomposed by source gas of ZrC bromide process, and influence on ZrC production shall be quite small.

Concerning this topic, an additional study on the thermochemical equilibrium calculation in case of ZrC coating on PuO_2 -YSZ fuel kernel is in progress (Ueta, et al., 2018). The interim result of the study indicates that a small amount of solid reactant, plutonium oxybromide (PuOBr), could be produced with ZrC, but any hazardous potentials of PuOBr to 3S-TRISO fuel kernel are unknown. A thin PyC coating as an intermediate layer between ZrC and fuel kernel could be a countermeasure against the reaction of the fuel kernel with the oxybromide (Ueta, et al., 2018).

Fig. 6 A calculation result on Factsage5.5.

Finally, it was concluded that YSZ or ZrC crystal might drop off from the specimen during the FIB treatment before STEM observation, and no deterioration of YSZ exposed by source gases of ZrC bromide process was confirmed. On the other hand, it is suggested that pore found at the boundary of ZrC coating and the fuel kernel as shown in Fig. 5b might induce disadvantages such as decrease of thermal conductivity and generation of interfacial crack due to increase of fission gas accumulated in the pore. The latter might not be a major problem because of the following reasons; at the first, ZrC as the oxygen getter would react chemically free oxygen generated in the kernel by fission even if some interfacial cracks exist in ZrC layer. At the second, even if the fission gas released from the kernel passes outside through the pore in ZrC coating, a low-density pyrolytic carbon layer which is the outer layer of ZrC can work as “buffer” to prevent the coated fuel particle from the failure due to excessive increase of internal pressure by the gas. However, reduction of pores at the boundary of ZrC coating is important to solve the former disadvantage above and to upgrade the ZrC coating technology. For the answer in the future, optimizing the coating condition, especially focused on the temperature at the beginning of ZrC coating, could be investigated in detail.

4. Conclusions

Interim results are reported on coating test and characterization of ZrC coating on YSZ dummy kernel for 3S-TRISO fuel for Pu-burner HTGR. ZrC layers with 18 - 21 μm of thicknesses have been obtained successfully with 0.1 kg of YSZ particle loading weight. It was confirmed that no deterioration of YSZ exposed by source gases of ZrC bromide process was observed by STEM observation. Examination on the relationship between material properties and coating conditions on ZrC such as gas flow rate, temperature, etc. is in the progress through upcoming ZrC coating tests.

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