



Fabrication of uniform ZrC coating layer for the coated fuel particle of the very high temperature reactor

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ABSTRACT

Fuel for the very high temperature reactor is required to be used under severer irradiation conditions and higher operational reactor temperatures than those of present high temperature gas cooled reactors. Japan Atomic Energy Agency has developed zirconium carbide (ZrC)-coated fuel particles previously in laboratory scale which are expected to maintain their integrity at higher temperatures and burnup conditions than conventional silicon carbide-coated fuel particles. As one of the important R&D items, ZrC coating process development has been started in the year 2004 to determine the coating conditions to fabricate uniform structure of ZrC layers by using a new large-scale coater up to 0.2 kg batch. It was thought that excess carbon formed in the ZrC layer under the oscillation of coating temperature would cause non-uniformity of the ZrC layer. Finally, uniform ZrC coating layer has been fabricated successfully by adjusting the time constant of the coater and keeping the coating temperature at around 1400 °C.

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1. Introduction

Current high-temperature gas-cooled reactor (HTGR) uses Triso-coated fuel particles as shown in Fig. 1. The Triso-coated fuel particle consists of a micro spherical kernel of oxide or oxycarbide fuel and coating layers of porous pyrolytic carbon (buffer), inner dense pyrolytic carbon (IPyC), silicon carbide (SiC) and outer dense pyrolytic carbon (OPyC). The principal function of these coating layers is to retain fission products within the particle. Particularly, the SiC coating layer acts as a barrier against the diffusive release of metallic fission products which escape easily through the IPyC layer and provides mechanical strength for the particle.

The very-high-temperature reactor (VHTR) is one of the most promising candidates for the Generation IV Nuclear Energy System [1]. The VHTR demands the gas outlet temperature of approximately 1000 °C for supplying electricity and process heat, e.g., for hydrogen production, as proposed in the Generation-IV International Forum [1]. The VHTR fuel is required to have excellent safety performance up to burn-ups of about 15–20% fissions per initial metal atom (FIMA) and fluences of 6×10^{25} n/m² ($E > 0.1$ MeV) [1]. Although SiC has excellent properties, it gradually loses strength due to neutron irradiation and mechanical integrity at very high temperatures, especially above 1700 °C, by thermal dissociation [2–4]. The SiC coating layer is also attacked chemically

by fission product palladium whose yield from ²³⁹Pu is about ten-fold that from ²³⁵U [5], which may become a considerable issue in low enriched uranium (LEU) fuel. In both cases, degradation of the SiC coating layer leads to extensive release of fission products from the Triso-coated fuel particles.

Zirconium carbide (ZrC) is known as a refractory and chemically stable compound, having a melting point of 3540 °C, and a eutectic melting point with carbon of 2850 °C. The ZrC coating layer is a candidate to replace the SiC coating layer of the Triso-coated fuel particles; the resulting particle is termed a ZrC Triso-coated fuel particle.

Japan Atomic Energy Agency (JAEA) has been developing zirconium carbide (ZrC)-coated fuel particle as an advanced particle. In the study performed from early 1970 to 1980s at the former JAERI (Japan Atomic Energy Research Institute), coating technique of ZrC on the surface of the fuel particle by bromide process has been developed. Coating conditions to obtain ZrC with uniform structure and with good stoichiometry, that is, C/Zr ratio of 1.0, were acquired by a small-scale coater with 10g-batch size [7]. It has been demonstrated that ZrC-coated fuel particles have much higher stability at high temperature than the present SiC-coated fuel particles. The ZrC-coated fuel particles did not fail until ~6000 s was reached at 2400 °C, while a few percent of the conventional SiC-coated fuel particles failed already by 2200 °C, and almost 100% instantaneously at 2400 °C [8]. Also, the ZrC coating layer has higher resistance to chemical attack by the fission product palladium than the SiC coating layer [6,9]. These results have made the ZrC

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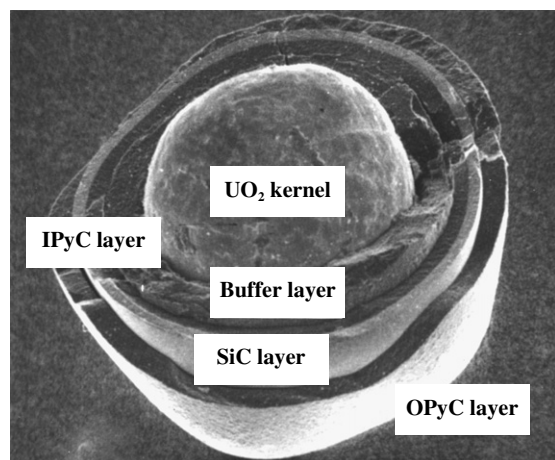


Fig. 1. Triso-coated particle fuel.

coating layer an interesting candidate to replace SiC for the advanced fuel particle.

The following investigations have been newly started since 2004 to establish the technology of fabrication and inspection methods for the ZrC-coated fuel particle at JAEA: (1) ZrC coating process development with a large-scale coater with 0.2 kg batch size, (2) inspection method development of ZrC-coated particles, especially with regard to C/Zr ratio (stoichiometry), ZrC coating layer density and ZrC failure fraction, and (3) irradiation test and post irradiation examination of ZrC-coated particles to characterize irradiation performance of the ZrC coating layer.

With regard to the ZrC coating process, it is necessary to obtain the coating condition for a larger scale coater than that of the previous study. The stoichiometric ZrC might be sensitive to the coating condition because of the complex reaction. When the scale of the coater is enlarged, *i.e.*, the volume of a fluidizing bed becomes large, the temperature distribution of coating region may change more easily. It would affect the stoichiometry of the ZrC layer.

The object of this paper is to determine the coating conditions to fabricate a uniform structure of ZrC layers through parametric tests by using the new large-scale coater.

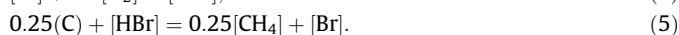
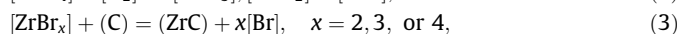
2. Experimental methods of ZrC coating

2.1. ZrC coating by bromide process

2.1.1. Chemical process

In previous studies in JAEA (former JAERI), some coating techniques of ZrC have been examined by the chemical vapor deposition (CVD) using zirconium halide vapors such as iodide, chloride and bromide [7]. From the experimental results, it was concluded that the bromide process was preferred to other halide processes experimentally, because it was found to be easier to produce a stoichiometric composition of ZrC.

In the bromide process, the ZrC coating layer is deposited with pyrolytic reaction of $ZrBr_4$, CH_4 and H_2 at about 1500 °C in a fluidized bed. Main reactions of the bromide process can be described as follows [7]:



(In above equations, solid and gas phases are expressed in parentheses and square brackets, respectively.)

2.1.2. Coating equipment

A new ZrC coater was constructed at Oarai Research and Development Center of JAEA as shown in Figs. 2 and 3. The ZrC coater was designed with the maximum batch size of 0.2 kg, which is about ten times larger than the previous device used.

The ZrC coater mainly consists of the gas supply equipment, the CVD coater, and the off-gas combustion equipment. In the gas supply system, liquid bromine is vaporized with argon as carrier gas at a temperature of 0 °C, and the bromine gas is introduced into the CVD coater from the bottom. A gas mixture of methane and hydrogen is also transferred into the coater. The CVD coater is composed of the lower and the upper heaters with in-line configuration to trigger ZrC reaction as described in Eqs. (1)–(4). The introduced bromine gas reacts with metallic zirconium sponge loaded in the lower heater, and then produces $ZrBr_x$ gases at about 600 °C. The upper heater has a particle fluidizing bed, and ZrC is coated on the surface of the particle at 1600 °C in the maximum. The off-gas treatment equipment removes soot, hydrogen bromide, and residual hydrogen.

2.1.3. Modification of the coater to larger scale

The ZrC coater was improved with regards to the safety operation and the temperature control to acquire the ZrC coating conditions for uniform structures in a large-scale coater. In a first step, the capacity of coating equipment was enlarged for up to 0.2 kg batch at the maximum to obtain the parameters for the coating condition for larger batch-sizes. Second, the temperature control system was improved. The temperature should be controlled in time with the reaction process because the bromide process is complexed as shown in Eqs. (1)–(4). Before the improvement of the coater, coating temperature was controlled by the temperature measurement inside the graphite tube from the ceiling of the coater by an infrared radiation thermometer. However, the soot produced in the off-gas often clouded the window for the thermometer located inside the coater, and caused a problem in the accurate measuring of the coating temperature. Therefore, the temperature control system was improved so that the coating temperature was controlled by the temperature measured at the outside surface of graphite tube with an infrared radiation thermometer. In this new system, controlled temperature is never disturbed by the off-gas etc.

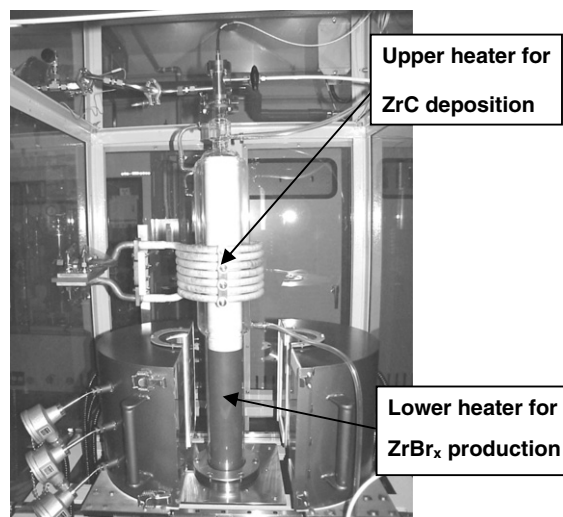


Fig. 2. Appearance of ZrC coater.

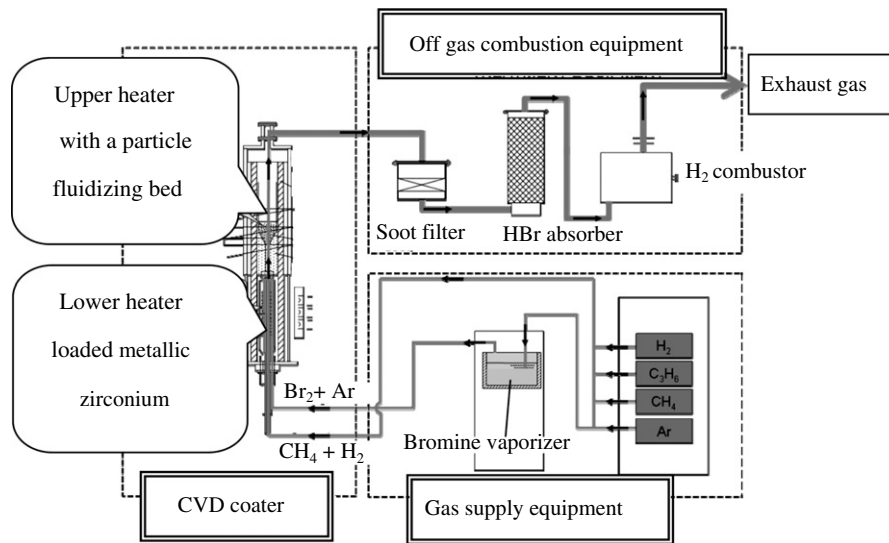


Fig. 3. Process flow diagram of ZrC coater.

2.2. Coating tests

The parametric tests for the conditions for ZrC coating were started, not only for obtaining a uniform ZrC coating layer by controlling the coating temperature, but also for ensuring the performance of the coater. In the parametric tests, non-nuclear surrogate particles were used. The particle consists of the micro spherical kernel of stabilized ZrO_2 and coating layer of dense PyC. Nominal diameter and density of the stabilized ZrO_2 particles were $720\ \mu\text{m}$ and $6.1\ \text{g/cm}^3$, respectively, similar to coated fuel particles containing the kernel and the buffer. The nominal layer thickness and density of the dense PyC were $35\ \mu\text{m}$ and $1.9\ \text{g/cm}^3$, respectively.

As the condition of the coater, the fluidizing bed with a 35 mm ID column with a 3 mm inlet nozzle was chosen. The range of the coating temperature and other coating conditions in the parametric tests have been set as shown in Table 1, which were determined based on results of the former research performed to acquire a stoichiometric ZrC coating layer [7].

2.3. Measurements for characterizations of the ZrC layer

The atomic ratio of carbon to zirconium was evaluated by measuring the density and the stoichiometry of the ZrC coating layer. The density of the ZrC coating layer was measured with a gas-pyc-

nometer, while the stoichiometry was calculated as the atom ratio of C and Zr, which were analyzed by the infrared light absorption during combustion in oxygen and by the inductively coupled plasma-atomic emission spectrometry (ICP-AES), respectively. For all measurements, the ZrC coating layer was removed from the IPyC layer by means of physical grinding. In the physical grinding technique, ZrC coating layer was grinded with quartz, and was separated in tetrabromoethane.

3. Results and discussion

3.1. Microstructure of the obtained ZrC coating layer

At the beginning of this research, ten ZrC coating tests were carried out. The thickness of coated ZrC layer was 10–30 μm . X-ray diffraction pattern indicated that the surface of the coated particle was ZrC. Fig. 4(a) shows the appearance of ZrC-coated particles.

However, as shown in Fig. 4(b), in the cross-section observation of ZrC layer, the non-uniform structures were observed as the circumferential stripes. In order to characterize these stripes in the ZrC layer, scanning transmission electron microscopy (STEM) observation and energy dispersive X-ray spectroscopy (EDX) analysis were carried out.

By the STEM observation, the dark-layered structures were observed in high angle annular dark field (HAADF) images as shown

Table 1
Condition of coating experiments

| Run | Temperature control ^a | Temperature ^b (°C) | Gas flow rate (l/min) | | | | Deposit rate (g/h) |
|-------------|----------------------------------|-------------------------------|--------------------------------|-----------------|----------------|-----|--------------------|
| | | | ZrBr ₄ ^c | CH ₄ | H ₂ | Ar | |
| ZrC-05-2002 | B | 1340–1500 | 0.0232 | 0.05 | 5.0 | 2.5 | 6.34 |
| ZrC-05-2003 | B | 1220–1550 | 0.0535 | 0.07 | 5.0 | 3.0 | 11.33 |
| ZrC-05-2004 | B | 1040–1520 | 0.0757 | 0.07 | 5.0 | 3.0 | 11.73 |
| ZrC-05-2005 | B | 1115–1441 | 0.0490 | 0.07 | 5.0 | 3.0 | 10.48 |
| ZrC-05-2006 | B | 1220–1540 | 0.0512 | 0.07 | 5.0 | 3.0 | 11.21 |
| ZrC-05-2007 | B | 1265–1488 | 0.0437 | 0.07 | 5.0 | 2.8 | 9.54 |
| ZrC-05-2008 | B | 1250–1540 | 0.0425 | 0.07 | 6.0 | 2.8 | 10.22 |
| ZrC-05-2009 | A | 1440–1496 | 0.0356 | 0.07 | 5.0 | 2.8 | 9.99 |
| ZrC-05-2010 | A | 1375–1480 | 0.0481 | 0.07 | 5.0 | 3.0 | 10.95 |
| ZrC-05-2011 | A | 1350–1450 | 0.0468 | 0.07 | 5.0 | 3.0 | 11.52 |

^a After (A) or before (B) improvement of temperature control.

^b Lowest temperature and highest temperature during coating run.

^c Calculated with the assumption that 100% of Zr be consumed by coating conversion to ZrBr₄.

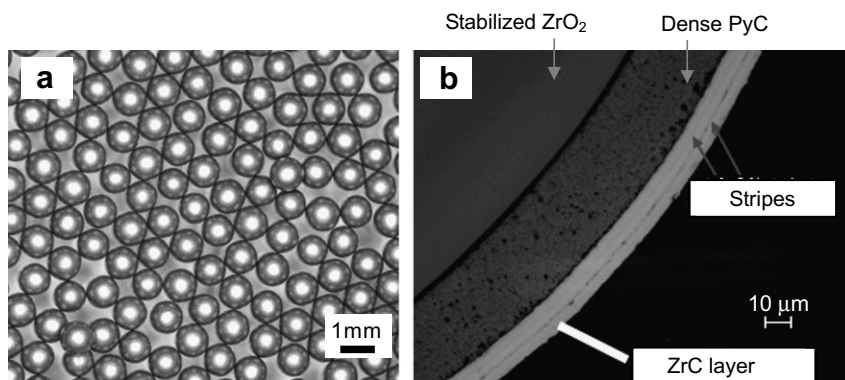


Fig. 4. Appearance (a) ZrC-05-2003 and cross-section (b) ZrC-05-2006 of ZrC-coated particle.

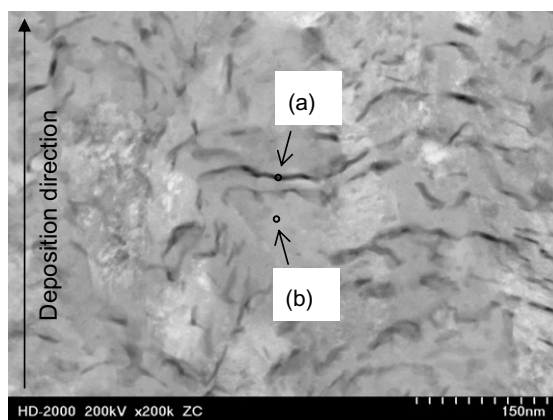


Fig. 5. STEM view in ZrC layer (ZrC-05-2003).

in Fig. 5 [11]. From this figure, it was indicated that the high-density regions designated as (b) and the low-density regions as (a) were layered with a relation to the deposition direction. It was seen that the dark-layered contrasts were distributed non-uniformly. It is thought that the circumferential stripes appearing in the optical microscopic image of the cross-section of the ZrC coating layer was caused by the non-uniform distribution of the layered structure.

To compare the composition of the each region, the EDX spectrum was investigated at the positions of (a) and (b) in Fig. 5. Figs. 6 and 7 show the spectra at the positions of (a) and (b), respectively. It should be noted that the Ti and Ga peaks were due to the specimen holder used in the experiment and the focused ion beam (FIB) preparation, respectively.

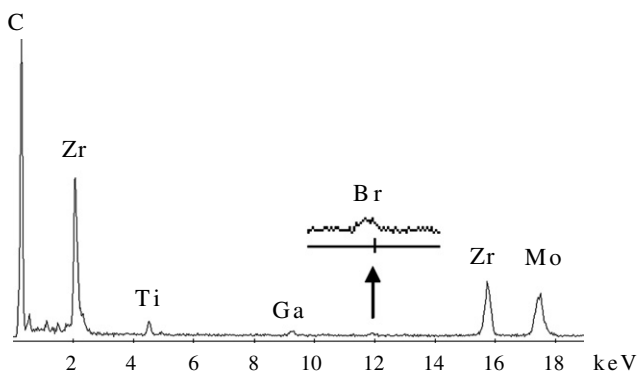


Fig. 6. EDX spectrum of the dark spot point (a) in STEM.

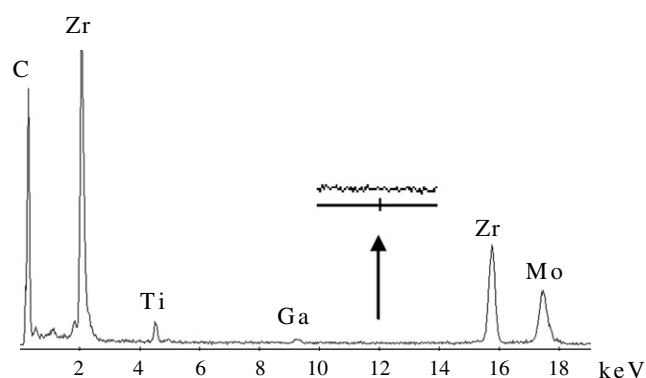


Fig. 7. EDX spectrum of the bright spot point (b) in STEM.

In the high-density region in Fig. 7, the C peak was lower than the Zr peak. On the other hand, in the low-density region in Fig. 6, the C peak was detected which was higher than the Zr peak. Furthermore, the Br peak was also found only in the spectrum of the low-density region.

From these results, it was suggested that the low-density region in the position (a) in Fig. 5 would be the area of segregated excess free carbon. In general, the existence of free carbon in ZrC layer makes not only the coating layer density lower but also the nominal C/Zr ratio higher. In fact, the density of the ZrC coating layer was measured as approximately 6.3 g/cm^3 , which corresponds to about 94% of the theoretical density (6.73 g/cm^3 [12]). The measurement of ZrC stoichiometry, *i.e.*, C/Zr ratio, resulted in a higher figure (1.2–1.3) than the stoichiometric ZrC (1.0).

From the viewpoint of the irradiation properties, it was reported that the retention of metal fission products by the ZrC + C layer was rather poor, presumably owing to a diffusion path through the free carbon phase [10]. Furthermore, it was presumed that the low-density region of ZrC due to the free carbon would contain Br inside it during the coating process. Therefore, the free carbon segregation areas in ZrC coating should be eliminated. From these results, the conditions of ZrC coating tests were examined.

3.2. Temperature dependency of non-uniformity in ZrC layer

The conditions of ZrC coating test in the present research were investigated based on the previous study performed in 1970s and 1980s. [7] The former research has shown that the coating temperature should be kept constant above $1350 \text{ }^\circ\text{C}$ to obtain stoichiometric ZrC [7]. In the present research, however, the coating temperature was oscillating over a range of 300° with time cycles of 5 min or less. For example, the coating temperature varied

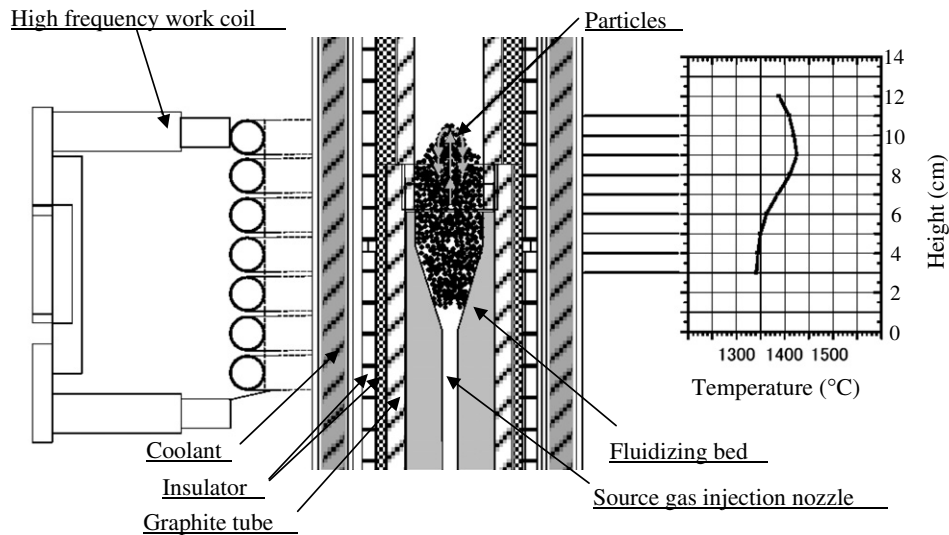


Fig. 8. Schematic and temperature distribution of ZrC coater at vertical direction.

between 1250 and 1540 °C while the set value was 1400 °C. In addition, in the region of the fluidizing bed, the difference between maximum temperature (at the top of the region) and minimum temperature (near the inlet nozzle) was about 100° as shown in Fig. 8. These data implied that the oscillation of the temperature during the coating process caused the circumferential stripes of free carbon in the ZrC layer.

The mechanism of the generation of excess carbon in the ZrC layer is discussed. In the bromide process of the ZrC coating technique, ZrC is deposited by supplying methane (CH_4) gas for C source and ZrBr_x gases for Zr independently into the fluidizing bed. Then, according to the previous research, it has been known that the efficiency of the pyrolysis of CH_4 gas is varied sensitively by changing the coating temperature [7]. The pyrolytic efficiency of CH_4 can be described by the weight ratio of carbon in the ZrC coating layer to carbon in the supplied CH_4 gas. Therefore, the amount of carbon supplied for ZrC coating increases when the pyrolytic efficiency of methane gas becomes higher. It is presumed that the pyrolytic efficiency of CH_4 of the present research corresponding to the coating temperature oscillation from 1250 to 1540 °C could vary in the range of 30–80% according to the previous result [7]. Therefore, it was suggested that at the beginning of the present research excess carbon was generated by the temperature oscillation which created the circumferential stripes.

3.3. Countermeasures to eliminate non-uniformity of the ZrC coating layer

To obtain uniformity of the ZrC coating layer, the coating temperature control during the ZrC coating test was improved with regard to the following points:

- (1) To diminish the oscillation of the temperature, the time constant of the coating temperature controller operation was shortened. Also, the position of the high-frequency coil for the graphite tube was adjusted so as to be on the same level with the location of the fluidizing particles.
- (2) To remove the generation of the excess carbon due to the frequent change of the efficiency of pyrolysis reaction of the methane gas (see reaction Eq. (1) in Section 2.1.1.), the condition to control the coating temperature was adjusted at 1400 °C according to the previous results [7], at which

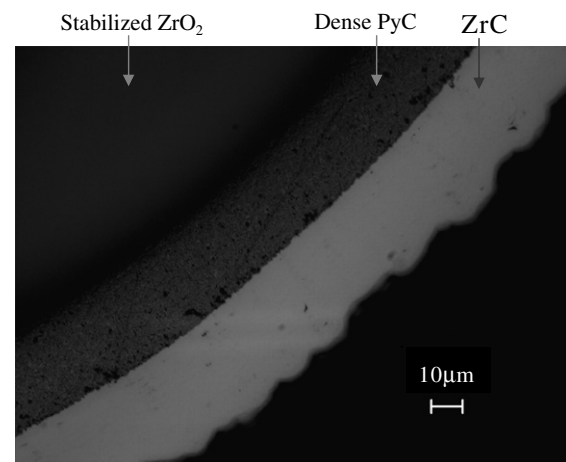


Fig. 9. Cross-section of ZrC layer after improvement (ZrC-05-2010).

the difference of the pyrolytic efficiency would be smaller even if the coating temperature varies.

By these countermeasures, the coating temperature variation has been reduced within 100 °C for the set value of 1400 °C, and the non-uniform structure in the ZrC layer was successfully eliminated as shown in Fig. 9.

4. Conclusion

JAEA started R&Ds to investigate the ZrC coating conditions under which uniform ZrC coating layers can be obtained by using the new large-scale coater up to 0.2 kg batch. ZrC coating layer was successfully obtained, however, at the beginning of this research, circumferential stripes were found in the cross-section of the ZrC coating layer. It was considered that the stripes came from the excess free carbon generated by the temperature oscillations during the coating process. It was found that coating temperature is very sensitive to produce the stoichiometric ZrC. To eliminate the non-uniform structure, time constant of coating temperature controller was adjusted to maintain the temperature at 1400 °C.

With these modifications, finally, a uniform ZrC coating layer was successfully obtained. Based on these results, continuous further improvements of coating method (ZrC onto PyC) and the development of appropriate characterization techniques of ZrC are underway at JAEA.

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