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Irradiation Sample Fabrications for VHTR
-Research and Development for Advanced High Temperature
Gas-cooled Reactor Fuels and Graphite Components-
(Contract Research)

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Irradiation Sample Fabrications for VHTR
- Research and Development for Advanced High Temperature Gas-cooled Reactor Fuels
and Graphite Components -
(Contract Research)

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Fuel for the Very High Temperature Reactor (VHTR) 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 the advanced silicon carbide (SiC) -coated fuel particles having thicker layer thicknesses, and zirconium carbide (ZrC)-coated particles that are expected to preserve their integrity at higher temperatures and burnup conditions than current conventional coated fuel particles. These particles have been fabricated successfully in order to perform irradiation tests at experimental reactors. This paper is summarized fabrication data of irradiation samples.

Keywords: Very High Temperature Reactor (VHTR), Advanced Silicon Carbide (SiC) -coated Fuel Particles, Zirconium Carbide (ZrC)-coated Particles, Irradiation Sample

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超高温ガス炉のための照射サンプル製造
- 革新的高温ガス炉燃料・黒鉛に関する技術開発 -
(受託研究)

日本原子力研究開発機構 原子力基礎工学研究部門
核熱応用工学ユニット
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(2008年12月10日 受理)

超高温ガス炉 (VHTR) の燃料は、現在の高温ガス炉より過酷な照射環境でかつより高温下で使用される。原子力機構は、現行燃料より優れ高温かつ高燃焼度に耐えうると期待される高性能で厚肉な炭化ケイ素 (SiC) 被覆燃料粒子や炭化ジルコニウム (ZrC) 被覆粒子を開発している。試験炉で照射試験を実施するための、これら高性能な炭化ケイ素 (SiC) 被覆燃料や炭化ジルコニウム (ZrC) 被覆粒子の製造に成功した。

本報は、照射試料の製造データをまとめたものである。

本報告書は文部科学省が日本原子力研究開発機構との(委託研究)契約により実施した研究(業務)成果に関するものである。

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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 to 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]. In the other side 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.

JAEA has planned to irradiate the advanced silicon carbide (SiC) fuels having thicker layer thicknesses at OSIRIS reactor in France near future. And also we have joined the irradiation tests of ZrC-coated particles both High Flux Isotope Reactor (HFIR) in Oak Ridge National Laboratory (ORNL) and High Flux Reactor (HFR) in The Nuclear Research & consultancy Group (NRG).

The object of this paper is summarized fabrication data for advanced SiC fuel and ZrC coated particles for VHTR developments.

2. Fabrication of advanced SiC-TRISO fuel

2.1 Fabrication processes of the VHTR fuel elements

The VHTR fuel fabrication process consists of three parts: (1) UO₂ kernels fabrication process, (2) PyC and SiC coating processes, (3) Manufacture process of Fuel compacts. These processes are described below.

2.2 UO₂ kernels fabrication process

The UO₂ kernels are fabricated in a gel-precipitation process. The process is shown in Fig. 2[5]. After formation of uranyl nitrate solution containing additives, spherical droplets are generated at the vibrating nozzles and fall into ammonia water to be aged to ammonium diuranate (ADU) particles. The reaction products of ammonium nitrate etc. are washed off, then the particles are dried and calcinated to UO₃ particles at 500°C in air. UO₃ particles are reduced and sintered to UO₂ particles with about 97%T.D. at 1600°C under hydrogen atmosphere[5].

2.3 PyC and SiC coating processes

Figure 3 [5] shows the fabrication flow diagram of coated fuel particles. Coating layers are deposited on the kernels in a chemical vapor deposition (CVD) process using a fluidized bed type of coater. The Tri-isotropic (TRISO) coating process is divided into four coating processes for the porous PyC, IPyC, SiC and final OPyC layers. Mixing gases of acetylene (C₂H₂) and argon (Ar) are used for the deposition of porous and low density PyC for the first layer; propylene (C₃H₆) and Ar for the deposition of dense PyC for the second and fourth layer; methyl-trichloro-silane (MTS) and hydrogen for the deposition of SiC for the third layer [5].

2.4 Manufacture process of fuel compacts

Figure 4 [5] shows the manufacture process of fuel compacts. First, natural graphite powder, electro-graphite powder and a binder are mixed, and then the mixture makes graphite matrix after fine grinding process. Coated fuel particles are over-coated with the graphite matrix and warm-pressed to make annular cylinder of green compacts. Green compacts are preliminarily heat treated for carbonization at 800°C under nitrogen atmosphere, then sintered at 1800°C under vacuum to make fuel compacts[5].

2.5 Specifications and Fabrication of advanced fuels for an irradiation test

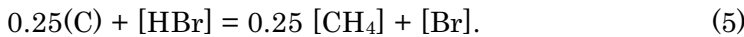
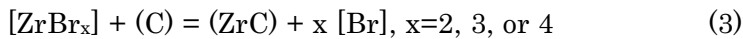
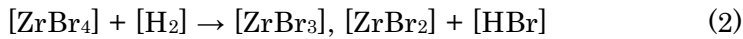
The Specifications of advanced UO₂ Kernel, coated fuel particle (CFP) and compact are described on Table 1 compared with first HTTR fuels. Advanced fuels are improved the SiC thicker layer thickness against a high internal pressure of FP and CO gases with higher burnup. Also the fuel kernel become smaller and a buffer become bigger against an accumulated gas pressure. The advanced SiC-coated fuels have been fabricated successfully at Nuclear Fuel Industries (NFI) based on the specifications and processes described above sections. A typical appearance of a fuel compact is shown at Fig.5. These fuels will be used the irradiation test at OSIRIS reactor near future for the VHTR developments.

3. Fabrication of ZrC coated particles

3.1 ZrC coating by bromide process

In previous studies in JAEA, some coating techniques of ZrC have been examined by the chemical vapor deposition (CVD) using zirconium halide vapors such as iodide, chloride and bromide [6]. 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 $1500^\circ C$ in a fluidized bed. Main reactions of the bromide process can be described as follows [6]:



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

3.2 Coating equipment

ZrC coater was constructed at Oarai Research and Development Center of JAEA as shown in Figs. 6 and 7. 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 $0^\circ C$, 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 $600^\circ C$. The upper heater has a particle fluidizing bed, and ZrC is coated on the surface of the particle at $1600^\circ C$ in the maximum. The off-gas treatment equipment removes soot, hydrogen bromide, and residual hydrogen.

3.3 Fabrication of ZrC coated particles for irradiation tests

To investigate the fundamental irradiation properties of ZrC, PyC and SiC using several irradiation temperatures under VHTR operating conditions, JAEA has joined the irradiation tests both HFIR in ORNL and HFR in NRG with the total of 18 kinds of particle samples. The fabricated irradiation samples are summarized at Table 2. These consist of Type 1) 5 kinds of inner IPyC /ZrC coatings with ZrO₂ kernels, Type 2) 4 kinds of IPyC/ZrC coatings with Al₂O₃ kernels, Type 3) IPyC/SiC/OPyC coatings with SiC kernels and Type 4) ZrO₂ and Type 5) Al₂O₃ kernels without coating and Type 6) 4 kinds of IPyC /ZrC/OPyC coatings with ZrO₂ kernels. The irradiation conditions 800 and 900 °C, 1100 °C and 1200 °C over $2 \times 10^{25} \text{ m}^{-2}$ of fast neutron fluences are selected for JAEA samples in the tests.

For the Type 1) and 2), 6) as shown in Fig. 8 [7], ZrC-coating layer is known as the most pronounced candidate for the advanced fuel particle used in VHTR. In the viewpoint of the coating material, it is essential for the ZrC coating layer to have the stoichiometric composition (of which the carbon to zirconium atomic ratio, (C/Zr) is nearly 1.0), because it shows higher performances with regards to a mechanical integrity, a thermal conductivity and a fission product retention under irradiations than those of one with C/Zr>1.0. The ZrC with C/Zr>1.0 has so-called free carbons as shown in Fig. 9. In the irradiation test, ZrC coatings with some different C/Zr ratio in the range of 1.0 to 1.3 are irradiated in order to study the irradiation effect on ZrC coatings, mainly for mechanical properties such as the hardness and strengths, for the microstructure of both ZrC and free carbons. In addition to the actual industrial viewpoint the coated fuel particle should be received a heat treatment to form the fuel compact, the heated ZrC coated particles at 1,800 °C are also irradiated to compare its behavior with non-heated ones.

The type 3) is SiC-TRISO particles with OPyC coating to compare PyC or SiC properties under the irradiation (a microstructure, PyC dimensional change, PyC anisotropy, etc.) with other samples. Types 4) and 5) are two substrate kernels used for JAEA samples in order to obtain the background data mainly for a dimensional change of each particle under the irradiation. For making PIEs easier, the some of these particles used highly purified Al₂O₃ kernels to reduce radioactivities comparing with ZrO₂ after the irradiation.

4. Conclusion

The advanced SiC-coated fuel particles have been fabricated successfully in order to perform irradiation tests at experimental reactors.

JAEA has developed 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 coated particles were successfully fabricated. These samples have been irradiated at experimental reactors.

Acknowledgements

The present study is the result of “Research and development for advanced high temperature gas cooled reactor fuels and graphite components” entrusted to the Japan Atomic Energy Research Institute by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). The authors are indebted to Dr. T. Ogawa, Dr. K. Minato and Dr. M. Ogawa from JAEA for their valuable advices, Mr. A. Yasuda of JAEA, Mr. T. Sekita and Mr. T. Ebisawa from Nuclear Fuel Industries, Ltd., Mr. T. Nemoto from Kaken Laboratory, Co. and Mr. T. Tobita from Nuclear Engineering, Co. for obtaining the experimental data, and Mr. T. Iyoku from JAEA for helpful comments in preparing this paper.

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Table 1 The specification of the Advanced fuel for irradiation tests planed at OSIRIS

Item	Advanced fuel	1st HTTR Fuel for reference	Sampling rate
<i>Fuel kernel</i>			
²³⁵ U enrichment (%)	9.9	3.4-9.9	1 sample/enrichment
Diameter (μm)	500	600	1 sample (50 particles) /fuel kernel lot
Sphericity	95% <1.2	95% <1.2	3 samples (100particles/sample)
Density (g/cm ³)	10.63	10.63	3 samples/fuel kernel lot
O/ U ratio	2.00	2.00	1 sample/fuel kernel lot
<i>CFP</i>			
Layer thickness Buffer (μm)	95	60	1 sample (50 particles) /CFP lot
I-PyC (μm)	40	30	1 sample (50 particles) /CFP lot
SiC (μm)	35	25	1 sample (50 particles) /CFP lot
O-PyC (μm)	40	45	1 sample (50 particles) /CFP lot
<i>Fuel compact</i>			
Packing fraction (%)	25	30	3 samples/ fuel compact lot
Dimensions			
Outer Diameter (mm)	10	26	All fuel compacts
Inner Diameter (mm)	2	10	All fuel compacts
Length (mm)	12	39	All fuel compacts

Table 2 Coated particles for irradiation tests at HFR and HFIR

No.	Type of particles	Particle D(μm)	Material	Size or thickness (μm)	Density (g/cm ³)	Remarks	lot	
1	ZrO ₂ +PyC+ZrC (ZrO ₂ kernel with 4.82% Y ₂ O ₃)	843	ZrO ₂	720(diameter)	6.07	C/Zr=1.11 as fabricated	ZrC-06-2022	
			PyC	35	1.9			
			ZrC	22	6.45			
2			Same as No.1 sample			C/Zr=1.11 heat treatment at about 1800 °C	ZrC-06-2022HT	
3			841	ZrO ₂	720(diameter)	6.07	C/Zr=1.03 as fabricated	ZrC-06-2048
	PyC	35		1.9				
	ZrC	28		6.5				
4*			Same as No.3 sample			C/Zr=1.03 heat treatment at about 1800 °C	ZrC-06-2048HT	
5*		858	ZrO ₂	720(diameter)	6.07	C/Zr=1.35 heat treatment at about 1800 °C	ZrC-06-2003HT	
	PyC		35	1.9				
	ZrC		21	6.01				
6	PyC+SiC (SiC kernel)	932	SiC	759(diameter)	Around1.9	as fabricated	91SiCCP	
	PyC		12	1.84				
	SiC		38	3.2				
	PyC		45	1.85				
7	ZrO ₂ with 4.82%Y ₂ O ₃	724	ZrO ₂	724(diameter)	6.07	heat treatment at about 1800 °C	ZCP-06-M01HT	
8						as received	ZCP-06-M01	
9	Al ₂ O ₃ +PyC+ZrC (99.99% Al ₂ O ₃ kernel)	902	Al ₂ O ₃	755(diameter)	3.89	C/Zr=1.1 as fabricated	ZrC-Al-2003	
			PyC	42	1.9			
			ZrC	24	6.5			
10				Same as No.9sample			C/Zr=1.1 heat treatment at about 1800 °C	ZrC-Al-2003HT
11			744	Al ₂ O ₃	642(diameter)	3.89	C/Zr=1.1 as fabricated	ZrC-Al-2001
	PyC	33		1.9				
	ZrC	9		6.5				
12			Same as No.11sample			C/Zr=1.1 heat treatment at about 1800 °C	ZrC-Al-2001HT	
13	Al ₂ O ₃ 99.99%	642	Al ₂ O ₃	642(diameter)	3.89	heat treatment at about 1800 °C	7001(600-710)HT	
14						as received	7001(600-710)	
15*	ZrO ₂ +IPyC +ZrC+OPyC (ZrO ₂ kernel with 4.82% Y ₂ O ₃)	895	ZrO ₂	720(diameter)	6.07	C/Zr=1.03 as fabricated	ZrC-07-3002	
			IPyC	35	1.9			
			ZrC	21	6.52			
			OPyC	24	1.9			
16*				Same as No.15 sample			C/Zr=1.03 heat treatment at about 1800 °C	ZrC-07-3002HT
17*		902	ZrO ₂	720(diameter)	6.07	C/Zr=1.03 as fabricated	ZrC-07-3010	
	IPyC		35	1.9				
	ZrC		27	6.52				
	OPyC		25	1.92				
18*			Same as No.17 sample			C/Zr=1.03 heat treatment at about 1800 °C	ZrC-07-3010HT	

* Irradiation samples both HFR and HFIR

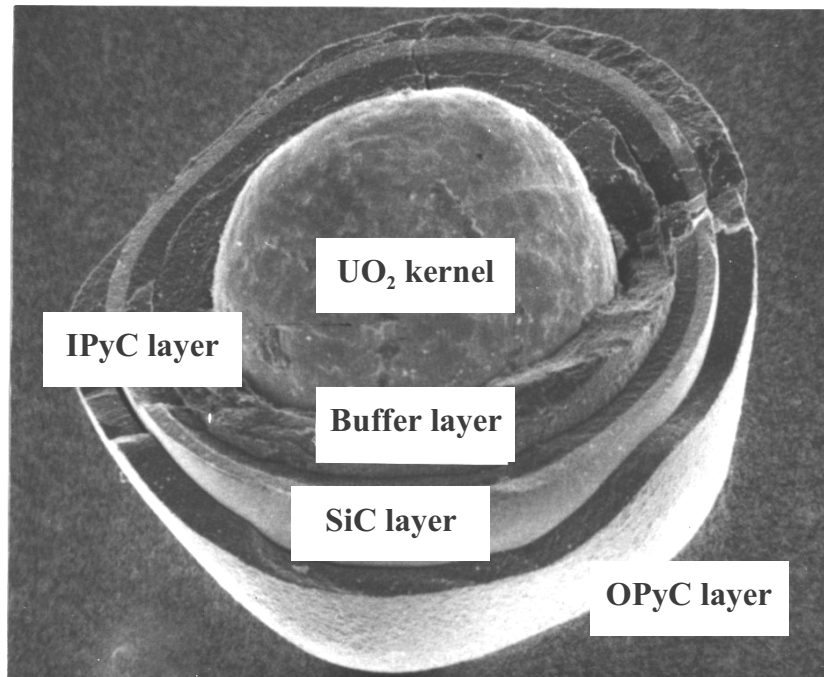


Fig. 1 Triso-coated particle fuel

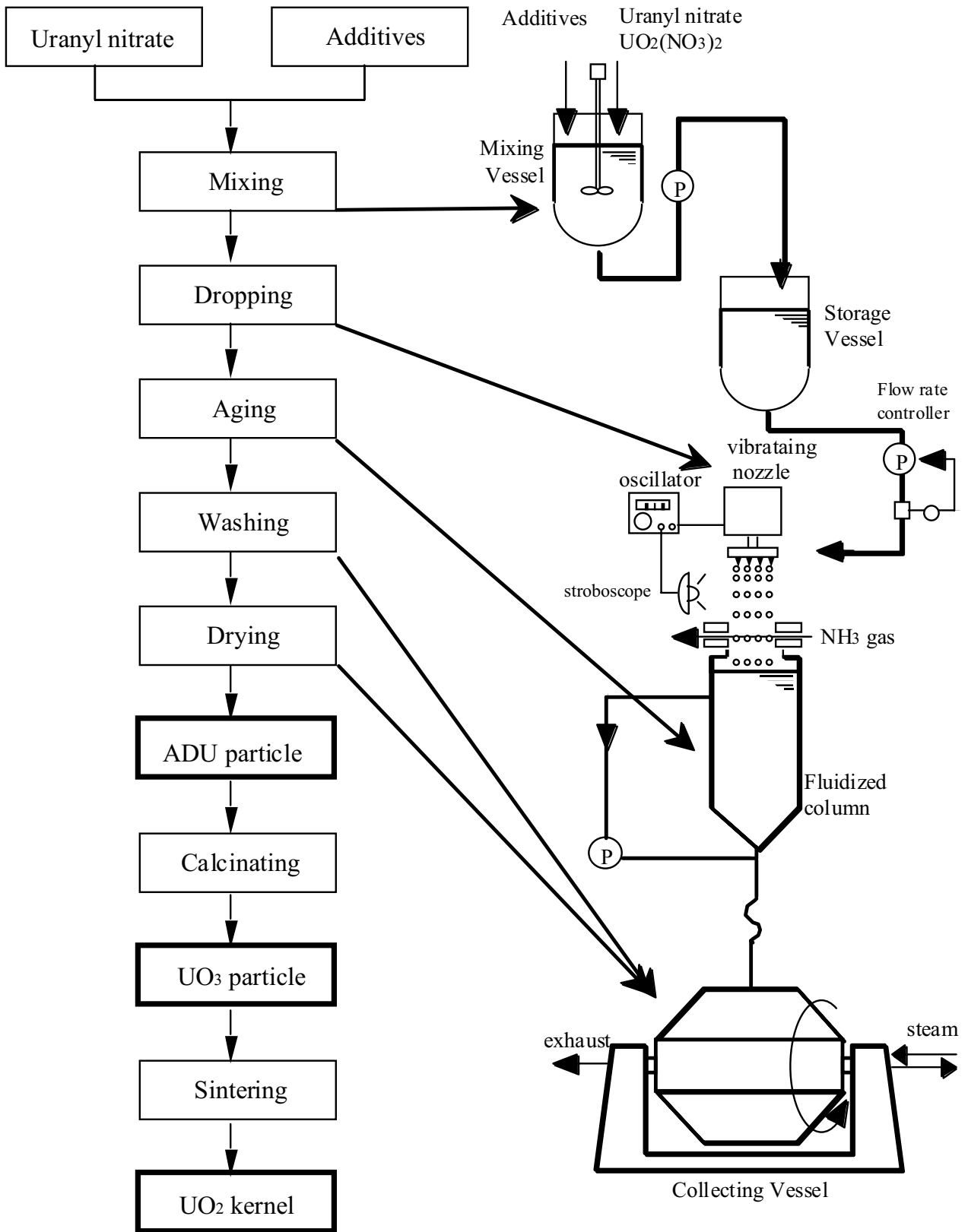
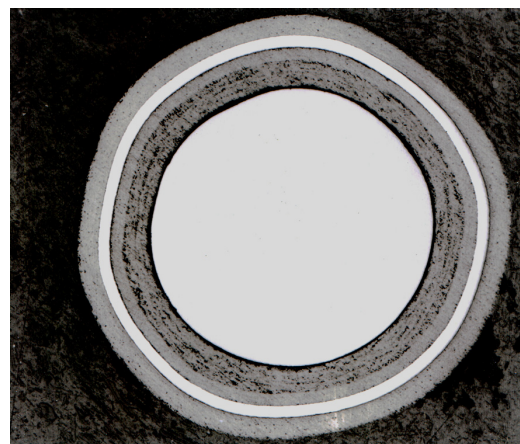
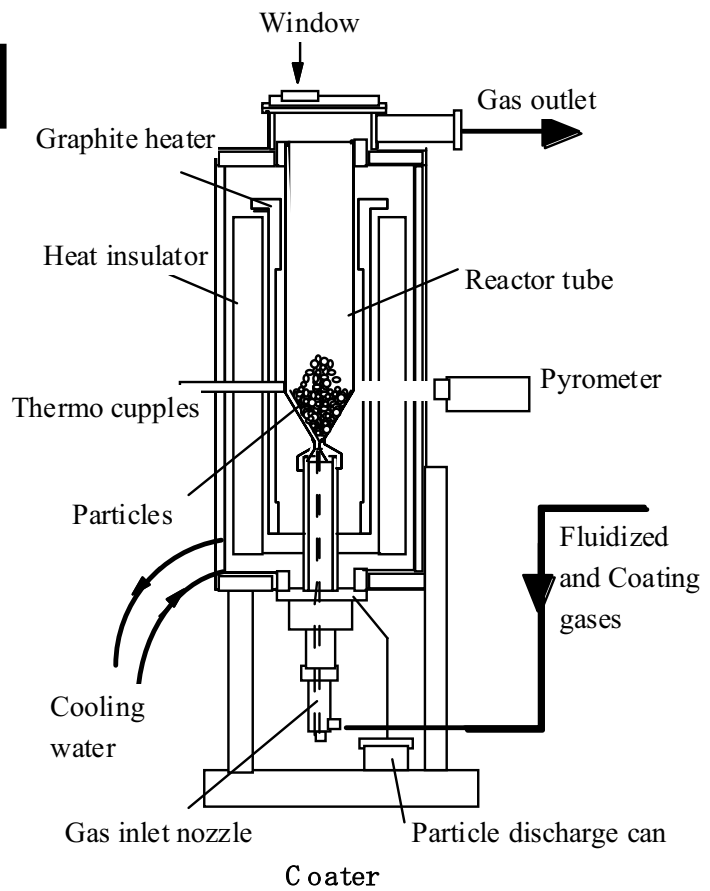
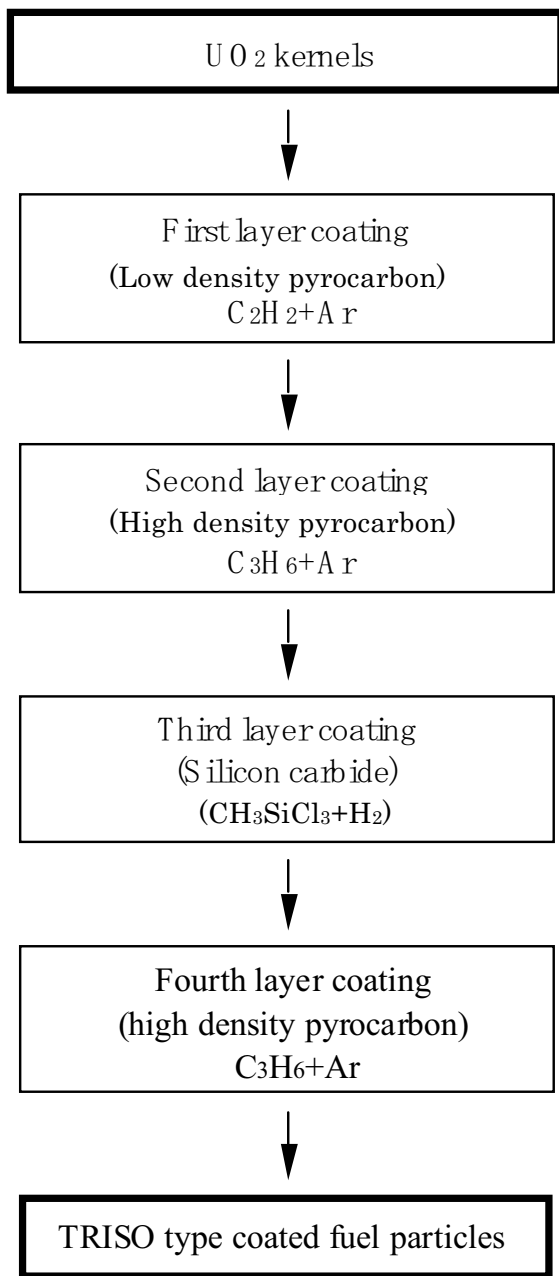


Fig. 2 UO_2 kernels fabrication process [5]



Polished cross section of coated fuel particle

Fig. 3 PyC and SiC coating processes [5]

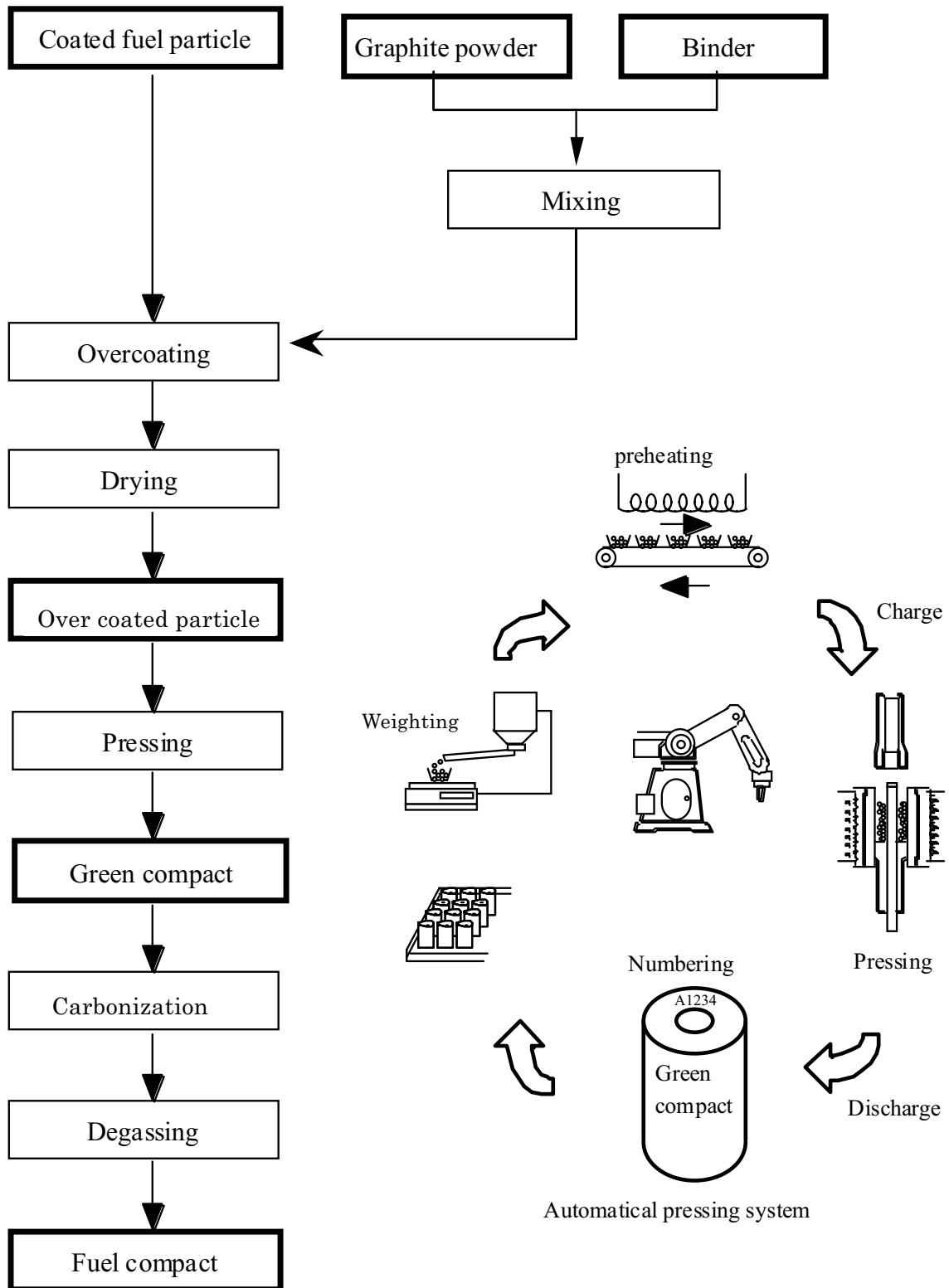


Fig. 4 Manufacture process of Fuel Compacts [5]



Fig. 5 Appearance of a fuel compact

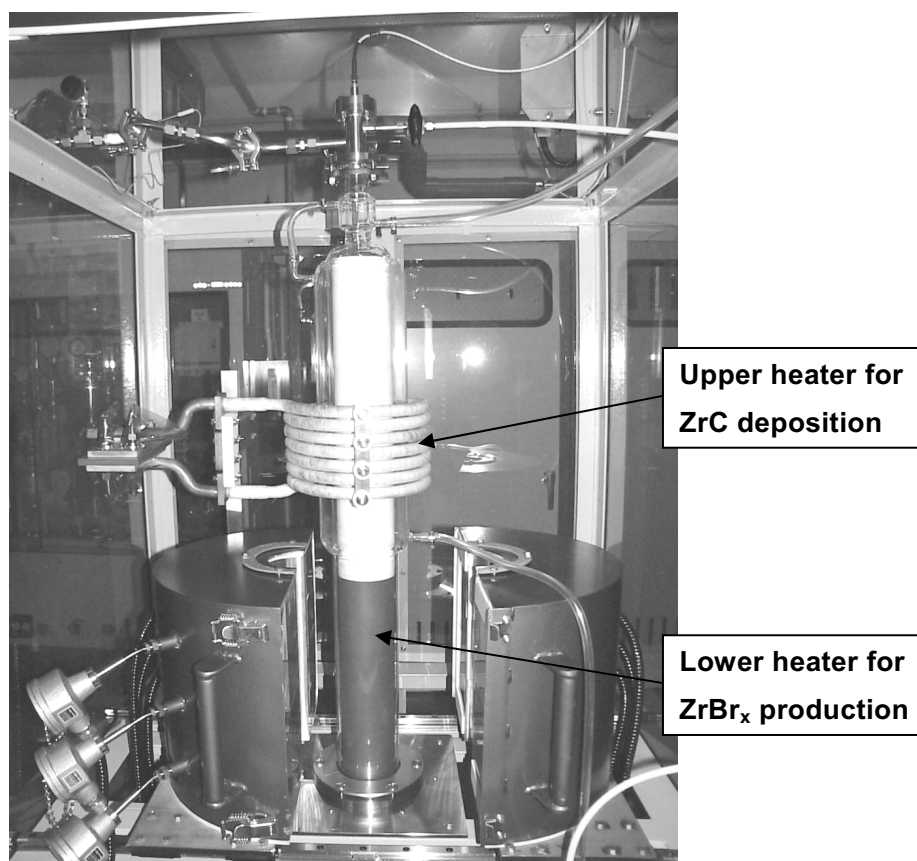


Fig. 6 Appearance of the CVD coater.

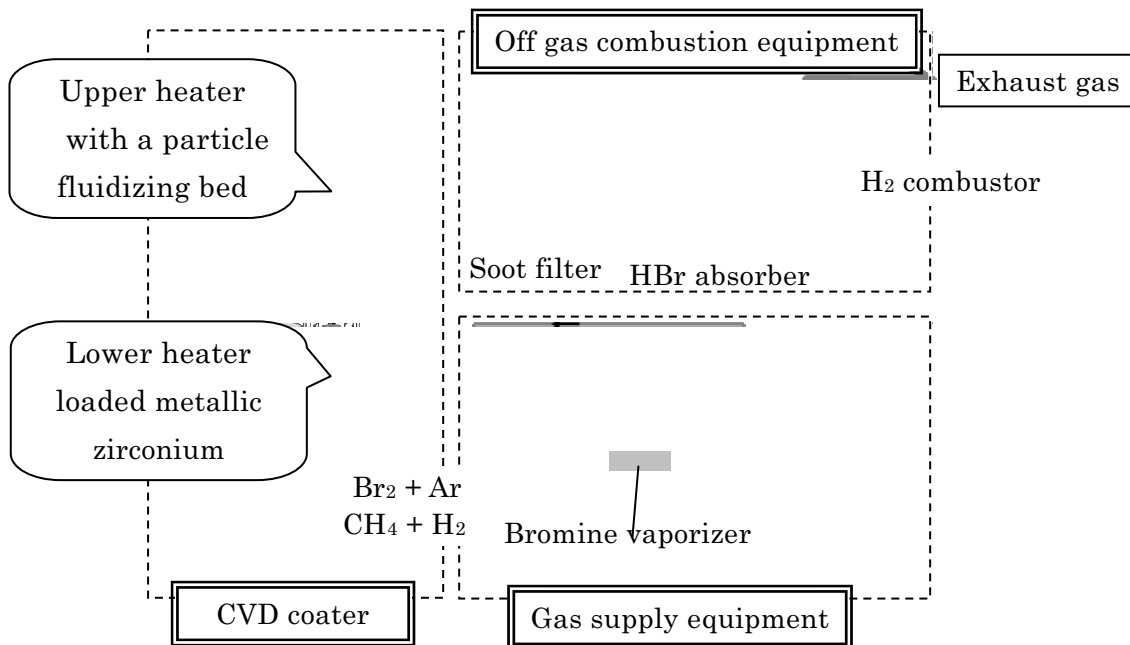


Fig. 7 Process flow diagram of ZrC coater.

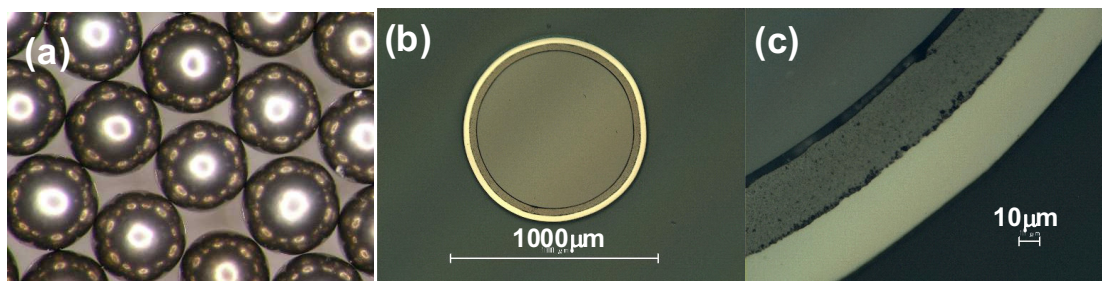


Fig. 8 (a) Appearance and (b) (c) cross sections of ZrC coated particles. [7]

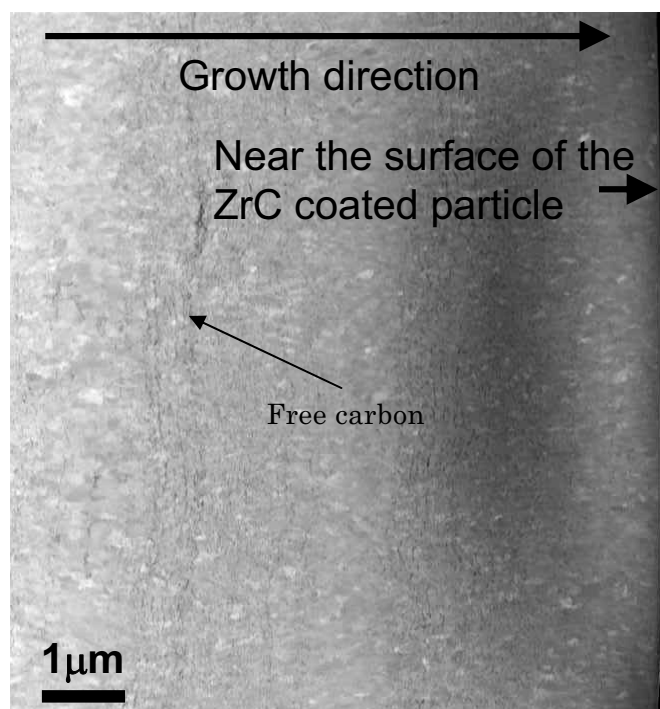


Fig. 9 STEM dark field (HAADF) image of ZrC coating layer with free carbon having high carbon peak by EDX

